



UNIT 16 CHEMICAL ENERGETICS

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COMBUSTION REACTION

EXOTHERMIC REACTION

STUDY GUIDE

This Unit has just two main components: the text and a television programme, 'Energy and rockets'. You will find notes about this programme in Section 8. You should try to read up to the end of Section 3 before watching although this is not absolutely necessary to understand the programme.

As with Unit 15 there is a CALCHEM program available for this Unit; it provides exercises and examples on Sections 2, 3, and 5.

I INTRODUCTION

In Unit 15 you were mainly concerned with questions like: what substances are formed in a reaction? How far will the reaction go—what is the equilibrium position? What happens when the equilibrium is disturbed in some way? This Unit examines a slightly different aspect of chemical reactions.

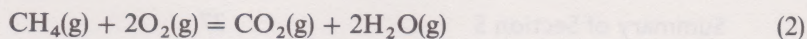
How do you heat your home and cook your food? What fuel do you use: is it natural gas or oil or perhaps a solid fuel, like coal or coke—or do you use electricity? Leaving aside electricity for a moment, what do you do with the fuel? Of course, you *burn* it in the oxygen in the air. More precisely, the characteristic and useful property of all these so-called 'fossil' fuels lies in their reaction with oxygen: chemical energy is *released* when they are burnt in oxygen. For example, coke is mainly carbon, and the combustion of carbon in oxygen, which can be represented by the chemical equation



results not only in the formation of gaseous carbon dioxide, but also in the release of energy in the form of heat and light. In the home, energy released in **combustion reactions** like this is generally used *directly* to heat something else; the air in your living room, the water in a saucepan on the stove or that circulating through the radiators; the food in your oven. At the time of writing, however, most forms of transport depend *indirectly* on the release of *chemical* energy in similar combustion reactions, as does the generation of most of our electricity.

But combustion in oxygen is just one sort of chemical reaction, and chemical reactions in general are accompanied by energy changes though they may be considerably smaller than in the examples cited above. We begin this Unit by examining the energetics of chemical reactions in this broader context, before returning (in Section 4) to take a closer look at chemical fuels.

You will also be concerned with a rather different, but related, question. When you turn on a gas tap, the gas does not immediately burst into flames. Indeed, a mixture of natural gas and air in your kitchen, or in any other container, will remain essentially unchanged for as long as you care to wait. It is common knowledge, however, that a tiny spark or match flame is sufficient to initiate a violent chemical reaction (Figure 1). The major ingredient of natural gas is methane, which has the formula CH_4 . It burns in oxygen to give carbon dioxide and water:



In the absence of a spark or flame, this reaction occurs so *slowly* that we do not even notice it.

This, then, is the question we shall examine in Section 5 of the Unit—the speed or *rate* of a chemical reaction, and how this is influenced by the reaction conditions. In many ways, this study is a necessary complement to the ideas developed in Unit 15. You have seen that a reaction can go only as far as the position of equilibrium dictates: later in this Unit you will examine some of the factors that govern *how fast* this equilibrium position is attained. To draw together these complementary strands, the Unit closes (Section 7) by examining an industrial process that has had a profound impact on our society—the Haber process for 'fixing' molecular nitrogen from the atmosphere.

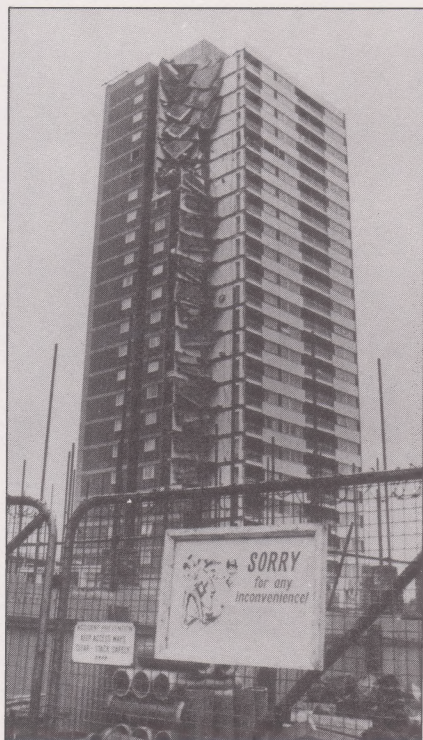
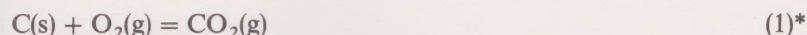


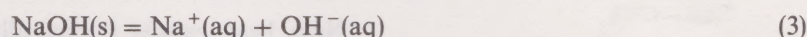
FIGURE 1 The Ronan Point disaster (1968), which was sparked off by the explosive reaction between methane and oxygen.

2 EXOTHERMIC AND ENDOTHERMIC CHEMICAL REACTIONS

All of the combustion reactions mentioned in the previous Section release energy in the form of heat: such reactions are described as being **exothermic** (from the Greek *exo* meaning outside and *therme* meaning heat). One of the examples cited earlier is the combustion of coke in oxygen, which can be simplified as:



This reaction obviously results in the release of a considerable amount of energy. By comparison, you would probably agree that dissolving solid sodium hydroxide in water, Equation 3, is a rather unexciting process:



However, as you may have noticed during Experiment 2 of Unit 15, when NaOH dissolves in water, the tube feels hotter. In other words, the process in Equation 3 results in a (fairly modest) temperature rise. This observation indicates that the dissolving process for NaOH is also exothermic; that is, it is accompanied by the release of energy, which heats up the solution.

The actual temperature rise produced by an exothermic reaction depends on many factors, for instance the conditions under which it takes place and how fast it goes. For example, the reaction between iron and oxygen to form iron oxide is an exothermic process. Nevertheless, your car does not get noticeably hotter as it slowly rusts by reaction with the oxygen in the atmosphere! More generally, if an exothermic reaction is carried out in an insulated container (such as a Thermos flask), the energy liberated will be slow to escape and the temperature may then become quite high. If the *same* reaction is performed under conditions in which heat loss is encouraged, a lower temperature will be produced. In addition, fast exothermic reactions tend to produce high temperatures because there is insufficient time for the energy released to be dissipated. (You will see some spectacular examples in the TV programme 'Energy and rockets'.) Slow exothermic reactions generally produce smaller temperature rises than fast ones.

Now, throughout the discussion of chemical equilibrium in Unit 15, you were interested in reactions taking place at *constant temperature*: you know how to write down the equilibrium constant for a reaction under these conditions. Moreover, you have seen that the equilibrium position, as characterized by the size of the equilibrium constant, depends on the temperature. For these reasons, chemists are mainly interested in the energetics of reactions at constant temperature. The one universal statement that it is possible to make about exothermic reactions is that if the products of such a reaction are finally obtained *at the same temperature* as the reactants, then heat must have left the reaction vessel. This is illustrated schematically in Figure 2.

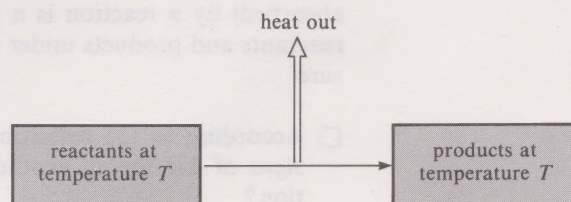
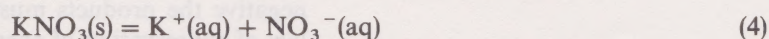


FIGURE 2 Schematic representation of an exothermic reaction at constant temperature.

- ☐ When potassium nitrate, KNO_3 , dissolves in water, the tube gets colder. This process can be represented by the following equation:



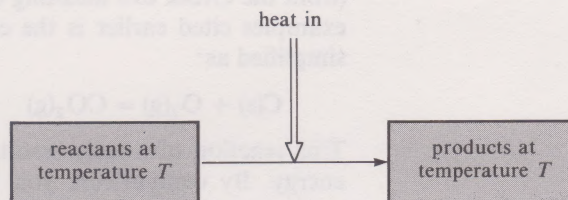
According to the discussion above, is this an exothermic process?

ENDOTHERMIC REACTION

ENTHALPY OF REACTION ΔH

PHASE CHANGE

FIGURE 3 Schematic representation of an endothermic reaction at constant temperature.



- No. The process represented by Equation 4 results in a *fall* in the temperature. According to the discussion above, heat must be *added* (not lost) in order to keep the temperature constant, so the process cannot be exothermic.

Reactions like this are described as being **endothermic** (from the Greek *endo* meaning within). Figure 3 shows a schematic picture of an endothermic process at constant temperature.

Now, heat transfer is generally symbolized by the letter Q . By convention, the value of Q for any process is defined as positive (greater than zero, >0) if heat is added to the system of interest (the reaction mixture, in this case), but negative (less than zero, <0) if heat is released to the surroundings.

- According to this convention, what is the sign of Q for an exothermic reaction? What about an endothermic process?
- To remain at constant temperature, an exothermic reaction must release heat to the surroundings, and vice versa for an endothermic reaction. The sign convention for heat transfer Q , suggests that:

for an exothermic reaction: Q is negative, $Q < 0$

for an endothermic reaction: Q is positive, $Q > 0$ (5)

As well as being at constant temperature, most reactions of interest to chemists, and indeed many natural processes as well, take place at constant pressure. Reactions you carry out in a beaker open to the atmosphere are essentially at constant pressure. Because of this, chemists have chosen to define a property that expresses the heat transferred under this condition. Thus, if a reaction takes place *at constant temperature and pressure*, the heat transferred is called the **enthalpy of reaction**, and is denoted by the symbol ΔH . Under these conditions,

$$\Delta H = Q \quad (6)$$

The symbol Δ (Greek capital delta) means a change in some physical quantity, in this case a change in *enthalpy*; that is

$$\Delta H = H(\text{products}) - H(\text{reactants}) \quad (7)$$

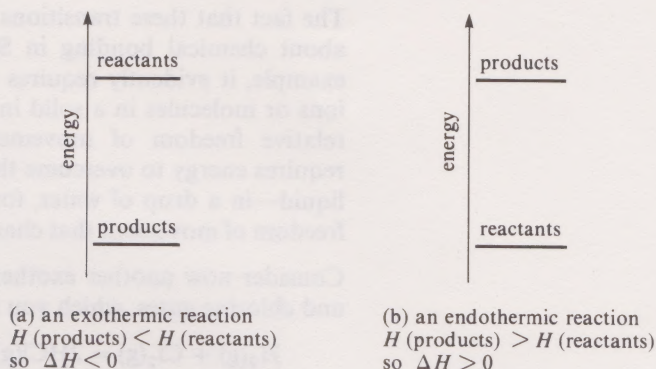
As implied above, enthalpy is just the most convenient kind of 'energy quantity' to describe changes at constant pressure, and throughout this Unit the terms enthalpy and energy will frequently be used interchangeably. Thus, you can read Equations 6 and 7 as saying that the heat released (or absorbed) by a reaction is a measure of the difference in energy between reactants and products under the same conditions of temperature and pressure.

- According to the definitions in expressions 5 and 6, what will be the *signs* of ΔH for an exothermic reaction and for an endothermic reaction?
- For an exothermic reaction: ΔH is negative, $\Delta H < 0$
For an endothermic reaction: ΔH is positive, $\Delta H > 0$ (8)

In summary, then, a reaction is exothermic if the enthalpy change ΔH at constant temperature is negative: according to Equation 7, for ΔH to be negative the products must be of *lower* energy than the reactants. By the law of conservation of energy (Unit 9), the energy lost must go somewhere, and you have seen that it results in heat being evolved. For an endothermic

reaction, the situation is exactly the reverse. So the relative energies of reactants and products in exothermic and endothermic reactions can be represented as shown schematically in Figure 4.

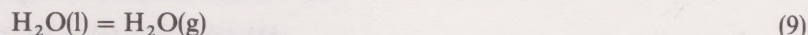
FIGURE 4 Schematic representation of (a) an exothermic reaction and (b) an endothermic reaction, defined in terms of enthalpy changes at constant temperature and pressure.



To make these ideas more concrete, consider a couple of familiar examples. You probably know that pure water boils at 100°C at normal atmospheric pressure. But does it continue to boil at this temperature as the heating is continued, or does the temperature of the water rise? If you have a suitable thermometer, you may like to try this experiment. You should find that the temperature remains constant until the last drop of water disappears. In other words, heat is supplied, but the temperature does not change.

What does happen?

The liquid (denoted by 'l') water disappears as gaseous water (steam) is formed. It seems that the *constant-temperature* process represented by Equation 9 *absorbs* energy: it is an endothermic process.



☐ What will be the *sign* of the enthalpy change for the process in Equation 9?

■ According to the discussion above, ΔH should be positive.

It is: experimentally, it is found to have the following value at 100°C :

$$\begin{aligned} \Delta H &= +43\,300 \text{ J mol}^{-1} \\ &= +43.3 \text{ kJ mol}^{-1} \end{aligned}$$

This example can be used to make two important generalizations. First, notice the unit, energy *per mole*: it requires 43.3 kJ to vaporize one mole (18 g) of water, 86.6 kJ for two moles, etc. In general, *the enthalpy change for a reaction depends on the amount(s) of reactant(s) consumed*.

ITQ 1 Suppose that you have a litre of pure water, which has just reached boiling temperature. How much energy is required to vaporize half this volume? Assume that 1 cm^3 of water has a mass of 1 g.

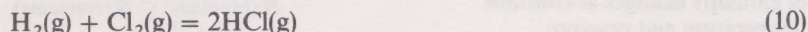
Secondly, the process represented by Equation 9 is one example of a class of similar processes known collectively as **phase changes**, sometimes called phase transitions. The term 'phase' simply means the physical states of a substance, be it solid, liquid or gas. In general, the transitions from solid to liquid (ice melting, for example), from liquid to gas (as you saw above) and, rather less common, from solid to gas,* all require energy: they are all endothermic processes.

* An example is provided by dry ice, which is solid carbon dioxide: this *sublimes* in air, that is it forms gaseous CO_2 directly. The fact that this process is endothermic accounts, in part, for the use of solid CO_2 as a coolant. It absorbs heat as it sublimates, and hence cools its surroundings. (It's also cold to start with, of course.) A second example is the sublimation of solid iodine, which probably caused iodine to leak from the bottle in your Experiment Kit.

ITQ 2 If you dab ether on your skin, it feels cold. Does this effect accord with the generalization made above?

The fact that these transitions are endothermic is consistent with the ideas about chemical bonding in Sections 6.4, 6.6 and 7 of Units 13–14. For example, it evidently requires energy to overcome the forces that hold the ions or molecules in a solid in their fixed positions, and hence to allow the relative freedom of movement that characterizes liquids. Similarly, it requires energy to overcome the forces that hold together the molecules in a liquid—in a drop of water, for instance—and hence to allow the complete freedom of movement that characterizes a gas.

Consider now another exothermic process, the reaction between hydrogen and chlorine gases, which you met in Unit 15:

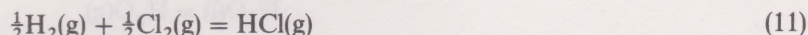


It is found experimentally that the reaction of one mole (2 g) of H_2 with one mole (71 g) of Cl_2 , at constant temperature and pressure, releases 184 kJ of heat.

☐ What is the enthalpy change for Equation 10?

■ $\Delta H = -184 \text{ kJ mol}^{-1}$

Notice that the enthalpy change is for the reaction *as written in Equation 10*: the value of ΔH represents the heat transferred when *one* mole of H_2 reacts with *one* mole of Cl_2 to give *two* moles of HCl . The ' mol^{-1} ' in the value, -184 kJ mol^{-1} , here implies that 184 kJ of heat are released *per mole of Equation 10*: it refers to the molar quantities implied by a particular equation. Thus if we choose to represent the reaction by the equation



the molar quantities implied by Equation 11 are halved relative to Equation 10.

☐ What is the enthalpy change for Equation 11?

■ $\Delta H = -92 \text{ kJ mol}^{-1}$; half the figure for Equation 10. The value tells us that 92 kJ of heat are released when *half* a mole of H_2 reacts with *half* a mole of Cl_2 to give *one* mole of HCl .

You should always remember that a value of ΔH refers to a particular chemical equation. The values that we have been quoting can be determined experimentally, although we do not go into that here. However, you will see in the next Section how enthalpy changes for certain types of reaction can be estimated in a rather simple way.

SUMMARY OF SECTION 2

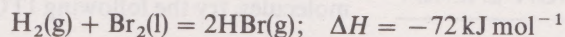
1 The enthalpy change ΔH for a chemical reaction is defined as the heat transferred under conditions of constant temperature and pressure.

2 Reactions can be classified according to the sign of ΔH , as either exothermic (ΔH negative) or endothermic (ΔH positive). At constant temperature, an exothermic reaction releases heat; the products are of lower energy than the reactants. For an endothermic reaction, the situation is exactly the reverse.

3 The enthalpy change for a reaction depends on the amount(s) of reactant(s) consumed.

4 In the case of phase changes, one can predict whether the process will be exothermic or endothermic.

SAQ 1 (a) Given the enthalpy change for the following reaction:



which of the following statements are true?

- (i) The reaction is endothermic.
- (ii) The reaction is exothermic.
- (iii) If the reaction is performed at constant temperature, heat will be released.
- (iv) If the reaction is performed at constant temperature, heat will be absorbed.
- (b) If 1 g of H_2 reacts completely with 80 g of Br_2 , and the temperature is held constant, how much heat will be transferred? (The relative atomic masses are $\text{H} = 1$ and $\text{Br} = 80$.)

SAQ 2 According to the discussion in Section 2, which of the processes (a) to (d) should be exothermic and which endothermic? Are there any of the processes for which it is not possible to decide on the basis of the discussion in Section 2?

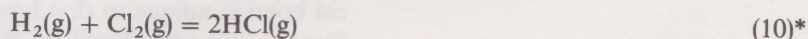
- (a) $\text{I}_2(\text{s}) = \text{I}_2(\text{g})$
- (b) $\text{NaCl}(\text{s}) = \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- (c) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) = \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
- (d) $\text{H}_2\text{O}(\text{l}) = \text{H}_2\text{O}(\text{s})$

SAQ 3 A scald from steam is generally more serious than one from contact with an equivalent amount of hot, even boiling, water. Can you suggest why this should be so?

3 ENTHALPY CHANGES ON THE MOLECULAR LEVEL

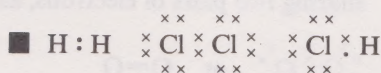
The previous Section introduced the vocabulary that chemists use when describing the energy changes associated with reactions. But why is it that some reactions are exothermic and others endothermic? Where does the energy come from or go to? In this Section we shall attempt to interpret the overall energy change for a reaction in terms of events on the molecular level.

Consider the simple gas reaction mentioned in Section 2:



As you saw in Units 13–14, gaseous hydrogen, chlorine and hydrogen chloride are all *covalent* substances: in the gas phase, each is composed of discrete diatomic molecules.

☐ Write down Lewis structures for the molecules H_2 , Cl_2 and HCl .



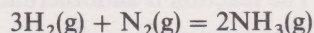
In each case, the molecule is held together by a single covalent bond, formed by sharing a pair of electrons, which, as you will remember from Units 13–14, can be represented more simply by a dash, as in $\text{H}-\text{H}$, for example.

- ☐ Look again at Equation 10. What changes take place on the molecular level when the reaction occurs?
- On the molecular level, the net effect of this reaction is to break $\text{H}-\text{H}$ and $\text{Cl}-\text{Cl}$ bonds, and form $\text{H}-\text{Cl}$ bonds.

BOND DISSOCIATION ENERGY

To get more practice with writing Lewis structures for simple gaseous molecules, try the following ITQ.

ITQ 3 List the bonds broken and formed in the following reaction:



Start by writing the Lewis structures for an N_2 and an NH_3 molecule. (The hydrogen and nitrogen atoms have electronic configurations $1s^1$ and $1s^2 2s^2 2p^3$, respectively.)

In general, chemical reactions of gaseous covalent compounds like those mentioned above involve breaking up reactant molecules and forming product molecules. The theme developed in this Section is that the energy released or absorbed during such a reaction results from a reordering of the way atoms are bound together, that is, from the breaking and making of chemical bonds.

3.1 BOND-BREAKING: BOND ENERGIES

Consider a molecule of hydrogen, H_2 . Now, under normal conditions, for example in hydrogen gas at room temperature and atmospheric pressure, molecules of H_2 do not simply 'fall apart' into hydrogen atoms. The pairs of hydrogen atoms are held together by chemical bonds, the result of powerful forces between the atomic pairs. It is, therefore, not surprising that it requires an *input* of energy to tear the two hydrogen atoms apart, that is, to 'break' the $\text{H}-\text{H}$ bond. The energy required is usually called the **bond dissociation energy** and denoted by the symbol D . Here we shall call it by the simpler name, *bond energy*. The particular bond under consideration is included in brackets after the D . So, in this case

$$D(\text{H}-\text{H}) = 7.24 \times 10^{-19} \text{ J per molecule}$$

However, the energy required to break one mole of $\text{H}-\text{H}$ bonds is a more useful quantity. This can be obtained by multiplying $7.24 \times 10^{-19} \text{ J per molecule}$ by the number of hydrogen molecules in one mole. This number is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$); that is

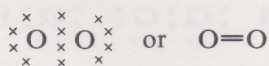
$$\begin{aligned} D(\text{H}-\text{H}) &= 7.24 \times 10^{-19} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} \\ &= 4.36 \times 10^5 \text{ J mol}^{-1}, \text{ or } 436 \text{ kJ mol}^{-1} \end{aligned}$$

This, then, is the energy required to break up one mole of molecular hydrogen to atoms.*

To generalize this idea a little: the bond energy associated with each chemical bond is unique to that bond. In the case of gaseous diatomic molecules like H_2 , this corresponds to the energy required to decompose the molecule into gaseous atoms. A few examples are given in Table 1.

□ Write a Lewis structure for the O_2 molecule.

■ As you saw in Units 13–14, oxygen has 6 electrons in its outermost shell. In O_2 , each oxygen atom can attain a noble gas structure by sharing *two* pairs of electrons, as:



Enter this last structure in the space provided in Table 1.

* With the simple representation $\text{H}-\text{H}$, it is tempting to think of the molecule as two atoms held together at a fixed distance. But this is not quite right. Spectroscopic measurements on molecules like H_2 indicate that the two atoms are not held rigidly apart at a fixed distance. This is why you may see the molecule represented as two masses (the H atoms) connected by a spring (Figure 5). The spring is flexible, and allows the two masses to move towards and away from each other. In other words, the molecule vibrates about some average separation. In terms of this 'spring model', you can think of the bond energy as the energy required to stretch the spring from its average length to the point where it snaps.

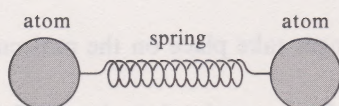


FIGURE 5 Ball-and-spring model of a diatomic molecule.

TABLE 1 Bond energies for selected diatomic molecules at 25°C

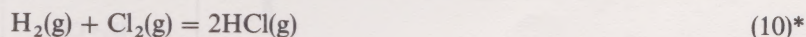
Molecule	Bond	$D/\text{kJ mol}^{-1}$
H_2	H—H	436
F_2	F—F	158
Cl_2	Cl—Cl	244
Br_2	Br—Br	193
I_2	I—I	151
HF	H—F	568
HCl	H—Cl	432
HBr	H—Br	366
HI	H—I	299
O_2		498
N_2	$\text{N}\equiv\text{N}$	945

Notice that in the cases of O_2 and N_2 (whose Lewis structure you used to answer ITQ 3), dissociation of the diatomic molecule corresponds to breaking *multiple* bonds, a double bond in O_2 and a triple bond in N_2 .

The values in Table 1 indicate, as you would expect, that the bond energy is a measure of the 'strength' of a particular bond (like the strength of the spring in Figure 5). For example, the variation of $D/\text{kJ mol}^{-1}$ in the series N_2 (945), O_2 (498), F_2 (158) clearly illustrates the greater strength of multiple bonds over single bonds in this group of elements, which are neighbours in the same row of the Periodic Table. The weakness of the F—F bond accounts, at least in part, for the extreme reactivity of fluorine. (The TV programme 'Energy and rockets' shows some spectacular reactions involving fluorine.)

3.2 THE USE OF BOND ENERGIES

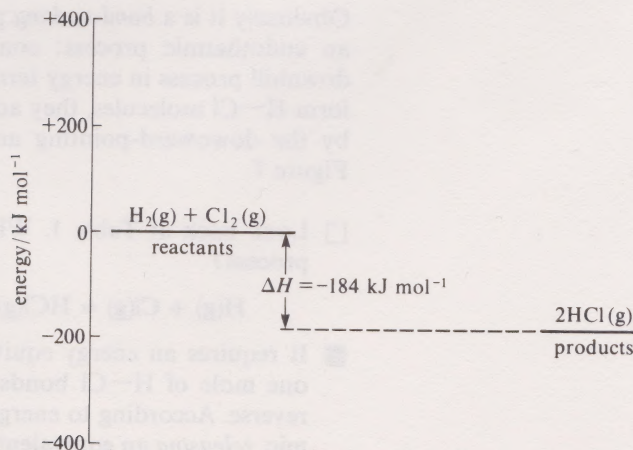
We said earlier that reactions of covalent compounds such as those mentioned in Section 3.1 involve breaking bonds and making new ones. The additional implication was that the energy changes associated with such reactions result from changes in the way atoms are bound together. To examine this idea more closely, consider again the simple gas reaction



for which the enthalpy change is

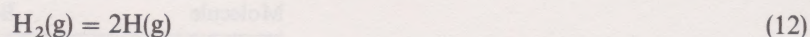
$$\Delta H = -184 \text{ kJ mol}^{-1}$$

The reaction is exothermic. This is shown schematically in Figure 6, where the energy of the reactants ($\text{H}_2 + \text{Cl}_2$) is taken arbitrarily to be zero. This convenient choice of the zero level is permissible because only energy *changes* are significant.

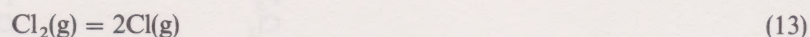
FIGURE 6 Energy diagram for the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) = 2\text{HCl}(\text{g})$.

HESS'S LAW

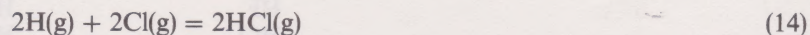
Now it is possible to think of this reaction proceeding by the following series of steps. First H_2 molecules and Cl_2 molecules are broken up:



and



Then the H and Cl atoms so formed are recombined to make HCl:



- ☐ What is the enthalpy change for the process in Equation 12?
- According to the discussion in Section 3.1, breaking the H—H bond in H_2 , requires an *input* of energy equivalent to the bond energy: it is an endothermic process, so taking the appropriate value from Table 1:

$$\Delta H(12) = D(\text{H}-\text{H}) = +436 \text{ kJ mol}^{-1}$$

Similarly, from Table 1 the enthalpy change for Reaction 13 is

$$\Delta H(13) = D(\text{Cl}-\text{Cl}) = +244 \text{ kJ mol}^{-1}$$

These steps, together with the overall reaction, are shown schematically in Figure 7. But what about the process in Equation 14, indicated by a question mark on the right-hand side of Figure 7? What kind of process is this?

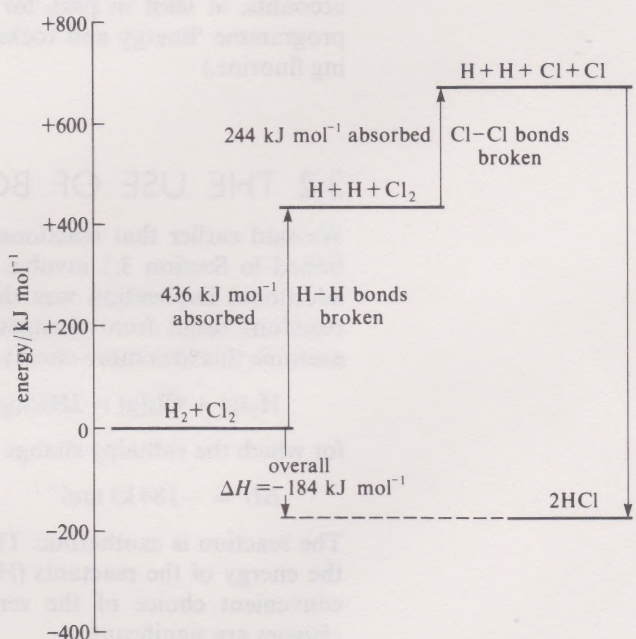
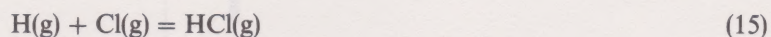


FIGURE 7 Relationship between bond energies and the overall enthalpy change of the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) = 2\text{HCl}(\text{g})$

Obviously it is a *bond-making* process. You have seen that bond-breaking is an endothermic process: conversely, bond-making between atoms is a downhill process in energy terms. When H atoms and Cl atoms combine to form H—Cl molecules, they achieve a state of *lower* energy. This is implied by the downward-pointing arrow that completes the overall reaction in Figure 7.

- ☐ Look back at Table 1. What is the enthalpy change for the following process?



- It requires an energy equivalent to $D(\text{H}-\text{Cl})$, that is, 432 kJ, to break one mole of H—Cl bonds. The process in Equation 15 is exactly the reverse. According to energy conservation, this process must be exothermic, *releasing* an equivalent amount of energy. Thus,

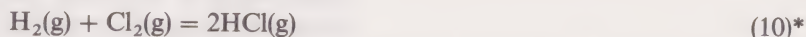
$$\Delta H(15) = -D(\text{H}-\text{Cl}) = -432 \text{ kJ mol}^{-1}$$

- What then, is the enthalpy change for the process in Equation 14?
- 432 kJ are released on formation of one mole of H—Cl bonds, so $2 \times 432 \text{ kJ} = 864 \text{ kJ}$ will be released when two moles are formed; that is

$$\Delta H(14) = -2D(\text{H—Cl}) = -864 \text{ kJ mol}^{-1}$$

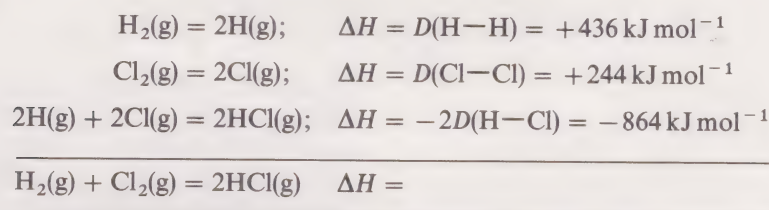
Write this value (that is, 864 kJ mol^{-1} released) against the right-hand arrow in Figure 7 if you wish.

Now the reaction of interest



is simply the *sum* of Equations 12, 13 and 14: the left-hand side, $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$, can be converted into the right-hand side, $2\text{HCl}(\text{g})$, either by the direct, one-step route of Equation 10, or by the three-step route of Equations 12, 13 and 14.

Now in Unit 9, you learnt that energy can be neither created nor destroyed. What this means in this context is that the enthalpy changes for the two routes must be equal. To prove this, imagine for a moment that it was not so. Then the conversion of hydrogen and chlorine into hydrogen chloride could be carried out by one route, and then reversed along the other, finishing with the hydrogen and chlorine one started with *plus surplus energy*. As this violates the law of conservation of energy, the enthalpy changes of the two routes must be equal: the values of ΔH for Equations 12 to 14 must add up to yield the value of ΔH for the overall reaction, Equation 10. Convince yourself that this is so by doing the sum below:



This important idea was established empirically by W. G. Hess in 1840. It is therefore called **Hess's law**, and may be stated as follows:

An energy change for a chemical reaction is the same whether the reaction takes place in just one step, or by a number of separate steps whose sum is equal to the one-step process.

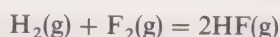
What you have just read should have convinced you that Hess's law is just a special case of the law of conservation of energy.

- Look again at Figure 7. How can the overall enthalpy change for Reaction 10 be related to the bond energies of the individual bonds that are broken and formed?
- The overall enthalpy change is the *difference* between the energy required to break the H—H and Cl—Cl bonds, and that released when the H—Cl bonds are formed:

$$\Delta H(10) = D(\text{H—H}) + D(\text{Cl—Cl}) - 2D(\text{H—Cl})$$

Try the following ITQ to check your understanding of this method for calculating enthalpy changes.

ITQ 4 Use appropriate bond energies from Table 1 to calculate the enthalpy change for the following reaction:



Does your calculation suggest a possible reason why this reaction is so exothermic?

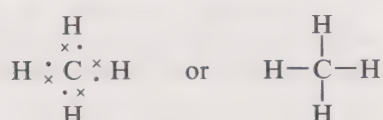
AVERAGE BOND ENERGY

These calculations incorporate a very important idea. When calculating enthalpy changes, it is not necessary to know whether or not, for example, the reaction in Equation 10 actually takes place as described above, that is, hydrogen and chlorine molecules first decomposing, and then the H and Cl atoms combining to form HCl molecules. Indeed, you will see later (Section 5) that this particular path is extremely unlikely. But here this is unimportant, because the *overall* energy change does *not* depend on the path actually taken.

So far, the discussion has concentrated on diatomic molecules, in which the bond energy is simply the energy required to dissociate the molecule. Each bond in a *polyatomic* molecule (NH_3 or CH_4 , for example) also has a characteristic bond energy associated with it, but in this case the energy is not quite as easy to pin down. The problem with polyatomic molecules is that the bond energy depends not only on the types of atom connected by the bond, and whether the bond is single, double, etc.; it also depends on the nature of the rest of the molecule, that is, on the bond's environment. Consider methane, CH_4 , for example.

□ Write a Lewis structure for CH_4 .

■ As you saw in Units 13–14, carbon has four electrons in its outermost shell, whereas hydrogen has one. In CH_4 , all the atoms can attain noble gas configurations by sharing pairs of electrons, as:



Thus, CH_4 contains four carbon–hydrogen bonds. The energies required to break successive C–H bonds in CH_4 are shown in Table 2: evidently, they are not all the same. However, you have seen how useful bond energies are in calculating ΔH for a reaction from the energies involved in breaking and making bonds. For this purpose, collections of **average bond energies** (for example, the average value in Table 2) are available, giving representative bond energies based on a large selection of compounds in which that bond appears. A few values of these are given in Table 3.

TABLE 2 Carbon–hydrogen bond energies in CH_4 at 25°C

Bond	$D/\text{kJ mol}^{-1}$
$\text{H}_3\text{C}-\text{H} = \text{H}_3\text{C} + \text{H}$	426
$\text{H}_2\text{C}-\text{H} = \text{H}_2\text{C} + \text{H}$	481
$\text{HC}-\text{H} = \text{HC} + \text{H}$	417
$\text{C}-\text{H} = \text{C} + \text{H}$	339
<hr/>	
average $\frac{1663}{4}$	≈ 416

TABLE 3 Some average bond energies at 25°C

Bond	Average bond energy/ kJ mol^{-1}
C—C	330
C=C	589
C \equiv C	811
C—H	416
C—Cl	326
C—O	327
C=O	804
O—O	143
O—H	463
N—N	159
N—H	391

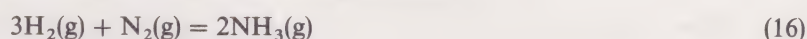
Notice that many of the bonds listed in Table 3 have carbon as one of the atoms involved. These are the kinds of bond present in the carbon compounds that you will study in Units 17–18. Several of these bonds will be referred to again during the discussion of chemical fuels in Section 4. Two of the other values listed in Table 3 are also worth a comment, namely the bond energies for the oxygen–oxygen (O—O) and nitrogen–nitrogen (N—N) *single* bonds. These bonds are present in the compounds hydrogen peroxide (H_2O_2) and hydrazine (N_2H_4), respectively. Convince yourself that this is so by trying the following ITQ.

ITQ 5 Write Lewis structures for H_2O_2 and N_2H_4 . Assume that the two oxygen or two nitrogen atoms are bonded to each other and that an equal number of H atoms are bound to each O or N.

The average bond energies for O—O and N—N can be compared with those for the corresponding multiple bonds in the diatomic molecules: from Table 1, $D(\text{O}=\text{O}) = 498 \text{ kJ mol}^{-1}$ and $D(\text{N}\equiv\text{N}) = 945 \text{ kJ mol}^{-1}$. In each case, the single bond is considerably weaker, and this has important consequences for the chemistry of compounds containing these bonds. The TV programme 'Energy and rockets' shows an example of this.

Average bond energies such as those in Table 3 can be used to calculate enthalpy changes in just the same way as before. Since they are average values, however, the resulting values of ΔH are only approximate. Nevertheless, they give a good indication of the magnitude of the energy changes involved. Consequently, in this Course, we shall often combine the strict bond energies of Table 1 with the average bond energies of Table 3 in the same calculation, using the symbol D for both.

For example consider the following reaction:



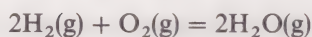
As you found in ITQ 3, this reaction involves breaking three H—H bonds and one N≡N bond for every six N—H bonds formed. Thus

$$\Delta H = 3D(\text{H—H}) + D(\text{N}\equiv\text{N}) - 6D(\text{N—H})$$

The required bond energies are given in Tables 1 and 3, so

$$\begin{aligned} \Delta H &= (3 \times 436 + 945 - 6 \times 391) \text{ kJ mol}^{-1} \\ &= -93 \text{ kJ mol}^{-1} \end{aligned}$$

ITQ 6 List the bonds broken and formed in the following reaction:



Start by drawing a Lewis structure for H_2O .

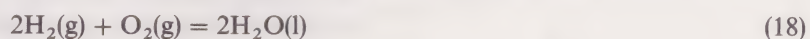
Using appropriate values from Tables 1 and 3, calculate the enthalpy change for this reaction.

3.3 LIMITATIONS ON THE USE OF BOND ENERGIES

The example in ITQ 6 highlights an important point about the use of bond energies: the calculation you performed refers to the following reaction:



in which *gaseous* water is formed. Suppose now that you wanted to calculate ΔH for the analogous reaction in which liquid water is formed:



In Section 2, you met the following process:



□ What is the enthalpy change for the reverse process, the condensation of gaseous water to liquid?



■ By the law of conservation of energy, this must be an exothermic process, releasing an equivalent amount of energy (cf SAQs 2 and 3), so

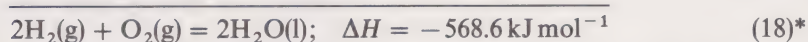
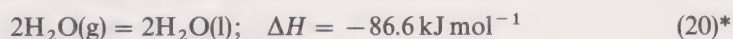
$$\Delta H(19) = -43.3 \text{ kJ mol}^{-1}$$

Can you see the connection between Equations 17, 18 and 19?

Equation 18 is the sum of Equation 17 and twice Equation 19. Remember that if an equation is doubled, then the value of ΔH must also be doubled:



According to Hess's law, the values of ΔH for Equation 17 and 20 must also add to give that for Equation 18:



This example shows quite clearly that the use of bond energies gives a reasonable estimate of ΔH only when all the reactants and products are gaseous species held together by simple covalent bonds. *Bond energies must be used carefully.* If the reaction of interest involves liquids (or solids) as well as gases, then this must be taken into account by including in the calculation values of ΔH for appropriate phase changes.

SUMMARY OF SECTION 3

1 The energy changes associated with simple gaseous reactions can be interpreted in terms of changes in the way the atoms are bound together.

2 Breaking a covalent bond requires an input of energy equivalent to the bond energy. Conversely, when atoms combine to form a bond, an equivalent amount of energy is released.

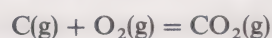
3 When calculating energy changes for chemical reactions, Hess's law is invaluable: it states that the energy change is the same whether the reaction takes place in just one step, or by a number of separate steps whose sum is equal to the one-step process.

4 Bond energies can be used to calculate the overall enthalpy change for a simple gas reaction involving either diatomic or polyatomic molecules (or both).

5 If the reaction of interest involves liquids (or solids) as well as gases, then values of ΔH for appropriate phase changes must be included in the calculation.

SAQ 4 This question leads in to the study of chemical fuels in the next Section.

(a) Write a Lewis structure for carbon dioxide, CO_2 . Then list the bonds broken and formed in the following reaction:



(b) Using appropriate bond energies from Tables 1 and 3, calculate the enthalpy change for the reaction above. Compare your answer with the value, $-393.5 \text{ kJ mol}^{-1}$, of ΔH for Reaction 1 in Section 1.

How do you account for any discrepancy between the two values?

SAQ 5 The decomposition of hydrogen peroxide, H_2O_2 , is an exothermic process. The energy released has been used for propulsion in space walks.

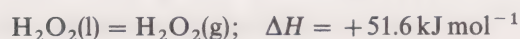
(a) Consider the decomposition of gaseous H_2O_2 :



Using appropriate bond energies from Tables 1 and 3, calculate ΔH for this reaction. (Refer back to the Lewis structures for H_2O_2 and H_2O , which you used to answer ITQs 5 and 6.)

Does your calculation suggest why this reaction is so exothermic?

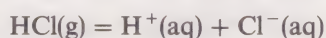
(b) Given the following enthalpy changes:



calculate ΔH for the decomposition of liquid H_2O_2 :



SAQ 6 Explain briefly why it is not possible to calculate ΔH for the following reaction from simple bond energy data:



4 CHEMICAL FUELS

As we said in the Introduction, most of the energy 'used' today comes originally from fossil fuels: coal, oil and natural gas. The characteristic property of such fuels lies in their reaction with oxygen in the air: energy is released when they are burnt in oxygen. So the concept of fuels and their energies really has to do with a 'fuel package', molecules to be burned, oxygen molecules 'to do the burning': a reshuffling of matter takes place at the molecular level, product molecules are formed and energy is released. For most conventional uses, chemical energy is first released as heat, which is either used directly or subject to several transformations. On purely chemical grounds, one of the main criteria of a 'good' fuel is the amount of heat that can be obtained when it is burnt, that is, the magnitude of ΔH for the combustion reaction.

Table 4 contains information on the combustion reactions of typical chemical fuels which are used in the internal combustion engine, in industry and the home, and in our bodies. It is evident from Table 4 that these fuels all burn in oxygen to yield the same two products, carbon dioxide and water. In order to compare the fuels, it has been assumed that the water formed is in the gaseous state, although this will not be the case for reactions occurring in the body. We shall now use the ideas developed in the previous Section to examine why such reactions are exothermic.

Let us start by considering one of the simplest examples in Table 4, the burning of natural gas (mostly methane), and try to interpret the overall energy change in terms of the bonds broken and formed.



☐ List the bonds broken and formed when Reaction 2 takes place.

TABLE 4 Combustion of typical fuels in oxygen*

Fuel and combustion reaction	ΔH	ΔH
	kJ per mol fuel	kJ per g fuel
carbon (coke)		
$\text{C}(\text{s}) + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$	-394	-33
methane (natural gas)		
$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) = \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	-800	-50
octane (petrol)†		
$\text{C}_8\text{H}_{18}(\text{l}) + 12\frac{1}{2}\text{O}_2(\text{g}) = 8\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{g})$	-5060	-44
stearic acid (in animal fats)		
$\text{C}_{18}\text{H}_{36}\text{O}_2(\text{s}) + 26\text{O}_2(\text{g}) = 18\text{CO}_2(\text{g}) + 18\text{H}_2\text{O}(\text{g})$	-10570	-37
glucose (in the body)		
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) = 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$	-2560	-14
hydrogen		
$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g})$	-241	-120

* The values given in this Table refer to combustion of the stated amount of *pure* fuel, for example, pure methane. The actual amount of heat that can be obtained from a given sample of petrol, natural gas, etc., depends very much on its chemical purity.

† Octane is just one of the many components of commercial petrol.

- Recalling the structures of CH_4 , O_2 , CO_2 and H_2O , four C—H and two O=O bonds are broken for every four O—H and two C=O bonds formed.

Gathering together information from Tables 1 and 3 gives:

	Single	$D/\text{kJ mol}^{-1}$	Double	$D/\text{kJ mol}^{-1}$
Broken	4 C—H	4×416	2 O=O	2×498
Made	4 O—H	4×463	2 C=O	2×804

- Use these values to check the value of ΔH for Reaction 2 given in Table 4.

■
$$\Delta H = (4 \times 416 + 2 \times 498 - 4 \times 463 - 2 \times 804) \text{ kJ mol}^{-1}$$
$$= -800 \text{ kJ mol}^{-1}$$

Notice that in this reaction the same numbers of single and double bonds are broken and made. However, although C—H and O—H bonds are of comparable strength, the C=O bond is over one and a half times as strong as the O=O bond.

Does this suggest why combustion of CH_4 is an exothermic reaction?

It seems that the exothermic nature of this reaction can be largely attributed to the extreme strength of the C=O bonds in CO_2 : considerable energy is released when these bonds are formed. It is often said that energy is 'stored' in natural gas. According to the molecular picture outlined above, a better description would be 'the fuel package (methane plus oxygen) is a source of energy because the combustion process yields a product with *stronger* bonds (higher bond energy).'

But what about the other combustion reactions in Table 4, excepting hydrogen for the moment?

Look back at Table 4. Can you see a problem with this simple analysis in terms of bond energies?

In the remaining reactions, the fuel is either a liquid or a solid. However, the phase changes from gas to liquid and from gas to solid are always exothermic (cf. the discussion in Sections 2 and 3.3), so hypothetical reactions involving *gaseous* fuels would in all cases be even more exothermic. If you are unsure about this, look back at the answers and comments to SAQs 4 and 5.

At first sight there seems to be another problem with the simple analysis outlined above: the numbers of bonds broken and made are not necessarily the same. Consider octane as an example. Like methane, octane is a member of a large class of compounds known as *hydrocarbons*. You will study the structures and properties of these compounds in detail in Units 17–18. For the moment, we ask you to accept that octane contains seven C—C bonds and 18 C—H bonds.

- With reference to the octane combustion reaction in Table 4, how many bonds are broken and made when gaseous octane is burned?
- Seven C—C, 18 C—H and $12\frac{1}{2}$ O=O bonds are broken for every 16 C=O and 18 O—H bonds made.

Thus, 34 bonds are made for every $37\frac{1}{2}$ that are broken (both totals including a number of multiple bonds). In other words, more bonds are broken than made, but the process is *still* highly exothermic. However, referring to the values in Table 3, you can see that both C—H ($D = 416 \text{ kJ mol}^{-1}$) bonds and C—C ($D = 330 \text{ kJ mol}^{-1}$) bonds are considerably weaker than the C=O bonds in CO_2 ($D = 804 \text{ kJ mol}^{-1}$). Again, it seems reasonable to

attribute the exothermic nature of this reaction to the extreme strength of the C=O bonds.

The structures of stearic acid and glucose are too complex to consider here. However, the combustion of these, and other *carbon* compounds in oxygen also yields carbon dioxide. It seems reasonable to conclude that the exothermic nature of such reactions results mainly from making the very strong C=O bonds at the expense of breaking weaker ones.

Notice that this argument does not apply to the combustion of hydrogen: H—H, O=O and O—H bonds are of comparable strength. In this case the decisive factor is the relative number of bonds broken (one H—H and a half O=O) and made (two O—H).

As a final point, consider the figures in the last column of Table 4. These were obtained by dividing the figures in the preceding column by the molar mass of the fuel in the given chemical equation. It is immediately apparent that on a weight-for-weight basis, hydrogen is by far the 'best' fuel, by a factor of three over petrol. This, together with the growing shortage of conventional fossil fuels and their associated pollution problems, has led to a considerable interest in the development of hydrogen as a synthetic chemical fuel. The photograph in Figure 8 suggests that at the time of writing, hydrogen-power is a very real possibility for the future.



FIGURE 8 The world's first hydrogen-powered mass transit vehicle, developed by the Billings Corporation of Provo, Utah, has demonstrated the feasibility and practicability of hydrogen as a fuel. This pollution-free, prototype bus safely stores hydrogen in small iron-titanium particles, which when heated supply hydrogen to the easily modified diesel engine.

The fuels discussed in this Section are all burnt in *oxygen* in order to release energy. The reason for using oxygen as the so-called 'oxidizer' is not hard to find: it is freely available in the air around us. But you have seen earlier in this Unit that combustion in oxygen is not the only type of exothermic reaction. Indeed, the simple analysis outlined in this and the previous Section suggests that any gaseous reaction will be exothermic if it results in the formation of strong bonds from weaker bonds. For example, as you found in answering ITQ 4, the weakness of the F—F bond explains why the reactions of many substances with fluorine are strongly exothermic.

However, fluorine is a thoroughly nasty material, and nobody in their right mind would suggest replacing oxygen with fluorine as the oxidizer for conventional uses. On the other hand, exotic, and often unpleasant, oxidizers and fuels are used in more specialized areas. One such area, the propellant systems used to power rockets, is examined in the TV programme for this Unit.

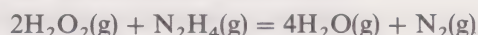
REACTION MECHANISM

SUMMARY OF SECTION 4

- 1 The energy obtained from most chemical fuels is the energy released in a reaction with oxygen.
- 2 An analysis using average bond energies suggests that the energy obtained from hydrocarbon fuels is high mainly because the C=O bond is much stronger than the O=O bond.
- 3 The combustion of a given mass of hydrogen releases much more energy than does the combustion of the same mass of other common fuels.

SAQ 7 As you will see in the TV programme 'Energy and rockets', the reaction between hydrogen peroxide (the oxidizer) and hydrazine (the fuel) was used to power the Messerschmidt 163.

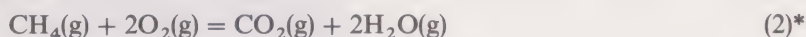
Calculate ΔH for the reaction



(Refer back to ITQ 5 for the structures of H_2O_2 and N_2H_4 .) Why is this reaction so exothermic?

5 RATES OF CHEMICAL REACTIONS

As the information in Table 4 showed, the combustion reactions discussed in the previous Section are all strongly exothermic. In addition, these highly exothermic reactions have equilibrium constants with truly enormous values at normal temperatures. For example, at 25 °C, the combustion of methane



has an equilibrium constant of about 10^{140} —an enormous number!

- ☐ What does this high value of K mean? (Refer back to Section 7 of Unit 15 if necessary.)
- ☒ The high value of K implies that *at equilibrium* reactants should be effectively completely converted into products.

Now oxygen is readily available from the atmosphere, and (leaving aside the water content of living organisms) we and all living things are composed of carbon compounds. Why then does not everything that is potentially flammable immediately burst into flame, including ourselves? As implied in the Introduction, the answer is that all such reactions are incredibly *slow* under normal conditions. They effectively never reach the very favourable equilibrium position.* Lucky for us!

In a similar way, the value of K for the reaction between gaseous hydrogen and chlorine (analogous to that between hydrogen and iodine, cf Unit 15 Sections 1 and 7):



implies that the *equilibrium* position strongly favours formation of the product, hydrogen chloride, under normal conditions. However, the size of K contains no hint of the experimental observation that a mixture of

* Referring again to Section 1, this is why you have to heat methane in order to fire it. This speeds up the reaction. Notice, however, that according to the discussion in Section 9 of Unit 15, changing the temperature will also change the value of K : in this case, K actually decreases with increasing temperature (it's about 10^{32} at 1000 °C). This point will be taken up in Sections 6 and 7.

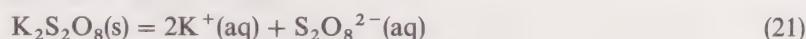
hydrogen and chlorine can be left for several days in a dark room with no noticeable reaction taking place, but that the mixture explodes violently when exposed *briefly* to a bright light.

It is fairly obvious that this aspect of chemical reactions is of crucial importance in the chemical industry. As you saw in Unit 15, the value of K for a reaction indicates the *maximum* yield of product that can be achieved, in principle, under a given set of conditions, but the examples cited above suggest that it says nothing about *how fast* this equilibrium position will be attained. From the equilibrium constant alone it is impossible to tell whether the reaction will take an inconveniently long time to reach equilibrium or whether it will proceed with explosive violence. It is evidently important to know not only how fast a reaction will go, but also how this speed or *rate* may be influenced or controlled by changing the reaction conditions.

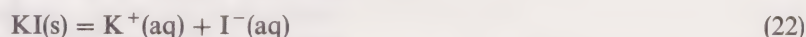
However, chemists have other interests in reaction rates apart from the problems associated with the chemical industry. In particular, the study of reaction rates provides one of the most powerful methods for testing models of what actually happens on the *molecular* level during a reaction: this is called the **reaction mechanism**. The theme to be developed here is that, unlike the equilibrium constant and the overall energy change for a reaction, the *rate* of a reaction depends on the *route* that it takes—on its mechanism.

5.1 WHAT INFLUENCES THE RATE OF A CHEMICAL REACTION?

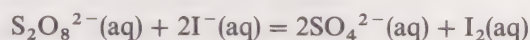
Two important ways of changing the rate of a chemical reaction can be demonstrated by mixing aqueous solutions of potassium persulphate, $K_2S_2O_8$, and potassium iodide, KI. In water $K_2S_2O_8$ forms the persulphate ion, $S_2O_8^{2-}(aq)$:



and KI forms the iodide ion, $I^-(aq)$:



Suppose that suitable aqueous solutions of these substances are quickly mixed to give one litre of a mixture which would, if no reaction occurred, contain 0.1 mole of KI and 0.01 mole of $K_2S_2O_8$. Now we have chosen these amounts because they give a convenient reaction rate: a reaction *does* occur, and the initially colourless mixture gradually turns brown. The persulphate and iodide ions gradually react together to form sulphate ions and iodine:



At 25 °C, with the concentrations specified above, the amount of iodine in the solution reaches 0.005 mole after about $1\frac{3}{4}$ minutes. At this moment exactly half of the iodine that would be produced by the *complete* reaction of the 0.01 moles of persulphate has been formed.

Suppose now that the reaction is repeated with the same mixture, but the temperature is 35 °C rather than 25 °C. This time, the 0.005 mole of I_2 appears after only about $\frac{3}{4}$ minute. A very similar result can be obtained in a different way: by doubling the initial concentration of persulphate. As before, the litre of mixture contains 0.1 mole of KI, but the amount of dissolved potassium persulphate, and therefore of $S_2O_8^{2-}(aq)$, is doubled to 0.02 mole. This time, 0.005 mole of I_2 is again formed after only about $\frac{3}{4}$ minute, even though the reaction temperature is only 25 °C.

These results illustrate something of great general importance. *The rate of a chemical reaction can often be increased by increasing the concentration of the reactants, or by raising the reaction temperature. Why should this be so?*

COLLISION MODEL OF A
CHEMICAL REACTION

ACTIVATION ENERGY

5.2 MOLECULAR INTERPRETATION OF THE
EFFECT OF CONCENTRATION AND
TEMPERATURE

Why should the rate of a reaction depend on the concentrations of the reactants, usually increasing as they are increased?

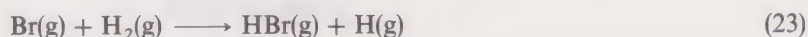
- ☐ What happens at the molecular level when the concentration of a substance is increased?
- Increasing the concentration increases the number of molecules in a given volume.

Intuitively, it seems reasonable to suggest that two molecules must meet or 'collide' before they react. According to this **collision model of a chemical reaction**, the rate of a reaction should be related to the frequency with which molecules collide—the *collision frequency*.

- ☐ If the number of molecules in a given volume is increased, would you expect the collision frequency to increase or to decrease?
- With more molecules in a given volume, you would expect collisions to occur more often, that is, the collision frequency should increase.

If the rate of a reaction increases with the collision frequency, then increasing the concentration of a reactant should increase the reaction rate. In other words, the collision idea fits our experimental findings in a qualitative way. To examine this collision model a bit more closely, we shall restrict the discussion to the simplest kind of process—gas reactions. As with the discussion of energy changes in Section 3, when a reaction occurs in solution, the presence of solvent molecules complicates the picture.

Consider the following particularly simple example, the reaction between bromine atoms and hydrogen molecules to produce hydrogen bromide molecules and hydrogen atoms:



Imagine a bromine atom moving around in a vessel containing hydrogen molecules. What factors will be important in determining how often it gets close enough to an H_2 molecule to collide? One factor is obviously the number of H_2 molecules in a given volume, that is, the concentration of hydrogen: this factor was discussed above. However, there is another factor, the relative speed of the bromine atom and the hydrogen molecules: the faster they move relative to one another, the more frequently they will collide. According to a collision model therefore, the rate of Reaction 23 will increase if this relative speed is increased.

Such an increase in relative molecular speed is just what is achieved by raising the temperature. From Unit 9 you know that the temperature of a gas rises when heat is transferred to it. The increase in energy brought about by heat transfer is shared among the individual molecules of the gas, principally in the form of kinetic energy.

- ☐ What is the relationship between the mass m of a molecule, its speed, v , and its kinetic energy E_k ?
- $E_k = \frac{1}{2}mv^2$ (Unit 9).

It follows that if the kinetic energy of a molecule increases, its speed, v , must increase: the net effect of increasing the temperature of a gas is to increase the *average* speed of the molecules. We stress the word *average*, because the molecules in a gas move at different speeds. Figure 9 represents the molecular model of a gas used in this Unit. The molecules move randomly with respect to one another. The arrows attached to the molecules mark directions of motion; their lengths are a measure of molecular speed. At any instant, the speed of some molecules is less than average; the speed of

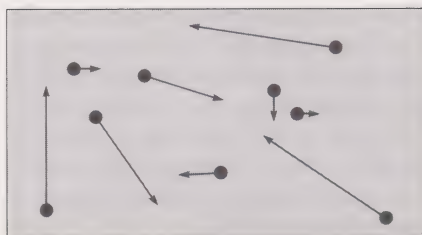


FIGURE 9 Atoms moving around randomly and independently in a gas.

others is greater. Moreover, kinetic energy is constantly being exchanged between molecules by collisions, so that a molecule moving quickly at one instant may be moving slowly at the next. Nevertheless, at any temperature, there will be a definite *average* speed, and this overall average is increased by a temperature rise.

In summary, the average speed of the molecules in a gas is greater at higher temperatures. In terms of the collision model, the collision frequency and hence the rate of reaction should increase with increasing temperature. Again this predicted behaviour agrees qualitatively with experimental findings: all gas reactions do go faster as the temperature is increased.

So far so good: in qualitative terms, the simple collision model predicts a dependence of reaction rates on concentration and on temperature which agrees in kind with the observed behaviour. However, there are problems with this simple model, which become apparent as soon as a more quantitative comparison is made between theory and experiment. By treating molecules as tiny spheres with a characteristic size and assuming that they travel at some *average* speed at a given temperature, it is possible to calculate the rate of collision as a function of concentration, temperature, etc. When such calculations are compared with the observed rate of a given reaction, important discrepancies become apparent. In particular, at a fixed temperature, the calculated rate of collision between molecules is often considerably higher than the observed rate of reaction, by a factor of 10^8 for Reaction 23 for example! It seems that the collision frequency provides an upper limit, and that, in general, most collisions do not lead to reaction.

Why should the reaction rate be lower than the collision frequency? Well, when two molecules collide, they may *either* react to form product molecules *or* they may rebound and go harmlessly on their way: in other words, not all collisions are equally effective in causing reaction. Why should this be so? A possible explanation is that molecules will react only if they collide with an energy equal to or greater than a certain minimum value. A gentle collision does not result in reaction; a violent collision does. Perhaps only those molecules that collide with an energy much larger than average can actually react. This suggests that there may be a *threshold energy* required to permit reaction, and that a collision leads to reaction only when the energy associated with it is equal to or greater than this threshold value.

This possible addition to the simple collision picture of chemical reaction would certainly provide a plausible explanation of why a proportion of collisions do not lead to reaction. Let us examine the idea in more detail.

5.3 THE ACTIVATION ENERGY

If most molecules do not possess enough energy to react, it must be because the energy threshold, known as the **activation energy** and given the symbol E_a , is greater than the average energy of a collision. However, from Section 5.2, you know that when the temperature is raised, the average kinetic energy of the gas molecules is increased. This in turn means that the proportion of collisions with an energy above the activation energy increases with temperature. Thus our modified collision model still predicts that the outcome of an increase in temperature is an increase in the rate of reaction.

This argument certainly agrees with the observed experimental behaviour. Moreover, although we shall not discuss it in detail here, by studying the variation in reaction rate with temperature, experimental values for the activation energies of reaction can be determined. For Reaction 23, for example, E_a is found to be about 82 kJ mol^{-1} .

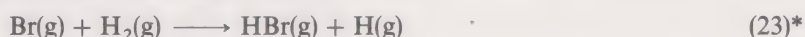
REACTION-COORDINATE
DIAGRAM

ACTIVATED COMPLEX

But does this picture of a threshold energy for reaction make sense? A good analogy is provided by the collision of one car with another:*

If (the cars) are both moving slowly, they'll bounce off each other and there will be no more damage than, possibly, heated emotions. If one of the cars is moving quite rapidly, however, there may be a significant rearrangement of the parts of each car. A bumper may be knocked off, the door from car A may leave the scene embedded in the hood of car B, and so on. It takes some minimum amount of energy though to break off a bumper and some different energy to wrench a door loose from its hinges. These would be the threshold energies for those particular automotive changes.

Similarly, for simple gas reactions, the reactant molecules are held together with covalent bonds: these must be broken, at least partially, before the atoms can be rearranged into product molecules—a process which you have seen requires energy. To examine this idea a bit more closely, consider again the very simple gas reaction



- What is the *overall* enthalpy change for Reaction 23? Is the reaction endothermic or exothermic?
- Overall, H—H bonds are broken and an equal number of H—Br bonds are formed. (Remember that you do not need to know the energies of the H and Br atoms: only changes in bonding are important.) Using bond energies from Table 1:

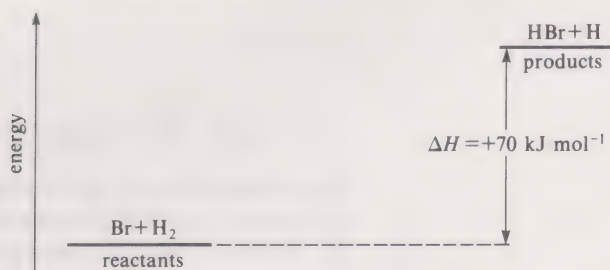
$$\begin{aligned} \Delta H &= D(\text{H—H}) - D(\text{H—Br}) \\ &= (436 - 366) \text{ kJ mol}^{-1} \\ &= 70 \text{ kJ mol}^{-1} \end{aligned}$$

The enthalpy change is positive, so the reaction is endothermic.

Recalling Figure 4b (Section 2), this overall energy change can be represented as shown in Figure 10: the enthalpy change for the reaction is the difference between the energy of the reactants and that of the products. But how does the energy change *during the course* of the reaction, that is, in the central part of the diagram in Figure 10?

Well, the 'reactant' level on the left-hand side of Figure 10 represents the situation when a bromine atom and a hydrogen molecule have a large separation: they do not influence one another. However, when a bromine atom gets quite close to a hydrogen molecule, it enters a region where repulsive interactions are strong enough to oppose any closer approach unless the system has enough energy to overcome these forces.

FIGURE 10 Energy diagram for the reaction
 $\text{Br(g)} + \text{H}_2\text{(g)} \longrightarrow \text{HBr(g)} + \text{H(g)}$.

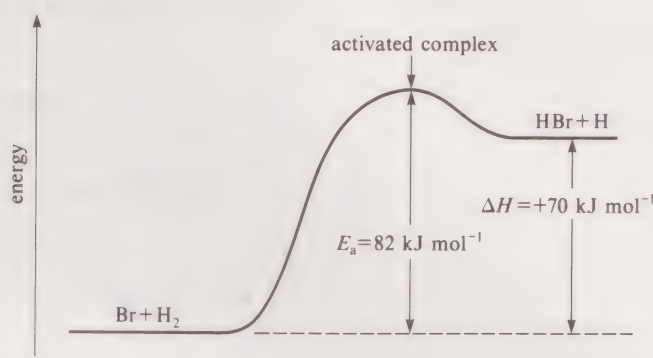


- Can you think of any repulsive interactions that might be present?
- In simple electrostatic terms, there will be repulsion between the negatively charged electrons of the Br atom and those of the H₂ molecule (and between the Br and H nuclei). Remember that charges of like sign repel one another (Unit 9).

* G. C. Pimentel and R. D. Spratley (1971) *Understanding Chemistry*, Holden-Day.

At the same time, the electrons of the H_2 molecule will start to be attracted by the bromine nucleus, and this will weaken the $\text{H}-\text{H}$ bond. This effect will continue until the system passes through an energy *maximum*, beyond which the bonding between Br and H increases, whereas that between H and H decreases to the extent that the situation is better described as an HBr molecule and an H atom: this situation is represented by the 'product' level on the right-hand side of Figure 10. Chemists like to represent this change pictorially by filling in the centre of the diagram as shown in Figure 11. Diagrams like this are called **reaction-coordinate diagrams**, because the horizontal axis is often referred to as the 'reaction coordinate', a term that is used to represent the progress of the reaction. Movement along the reaction coordinate from left to right is equivalent to those gradual changes that occur in the distances between the bromine atom and the two hydrogen atoms as the reactants change into the products.

FIGURE 11 Reaction-coordinate diagram for the reaction



The state of the system when the energy is a maximum corresponds to a hypothetical arrangement in which reactant bonds are partially broken and product bonds are partially formed, an arrangement that is often called the **activated complex**. For this particular reaction, the structure can be represented as follows



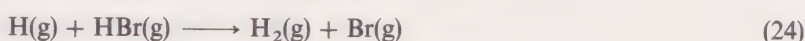
where the broken lines imply partial bonding (fewer than two electrons shared between two atoms): the position of the activated complex is shown on Figure 11. In general, however, it is not possible to predict the exact structure of the activated complex, other than that it represents a transition between reactants and products.

According to this pictorial representation, the difference in energy between the reactants and the activated complex is the activation energy for the reaction, also shown on Figure 11. Thus, E_a can be thought of as an *energy barrier* that reactant molecules must surmount before products can be formed. For reaction to take place, a bromine atom must collide with a hydrogen molecule and the joint system must have energy E_a more than the average energy of Br and H_2 ; otherwise it cannot cross the energy barrier.

Not only does Figure 11 give a pictorial view of the activation energy as an energy barrier to reaction, but it also illustrates an extremely important point, which was mentioned frequently in Section 3: the overall energy change, ΔH , does *not* depend on the size of the energy barrier, that is, on the path the reaction takes.

The example discussed so far, Equation 23, is an endothermic reaction. For simple endothermic processes like this, the reaction-coordinate diagram will always have the general shape shown in Figure 11, although the size of ΔH and of the energy barrier will, of course, vary from reaction to reaction. But what about exothermic reactions?

The first example to hand is the reverse of Equation 23:



□ What is the value of ΔH for Reaction 24?

CATALYST

- By the law of conservation of energy, the reaction must be exothermic, releasing an equivalent amount of energy, so

$$\Delta H(24) = -70 \text{ kJ mol}^{-1}$$

Now, according to the treatment in this Unit, the activation energy of a reaction must be positive.

- Before reading further, try to sketch a reaction-coordinate diagram showing the energy changes during the course of Reaction 24. Mark on your diagram the activation energy, E_a , the overall energy change, ΔH , and the position of the activated complex.
- As ΔH is negative, the products must be of lower energy than the reactants. The activation energy is the difference in energy between the reactants and the activated complex: if E_a is positive, there must again be a 'hump' in the middle of the diagram. A sketch is shown in Figure 12.

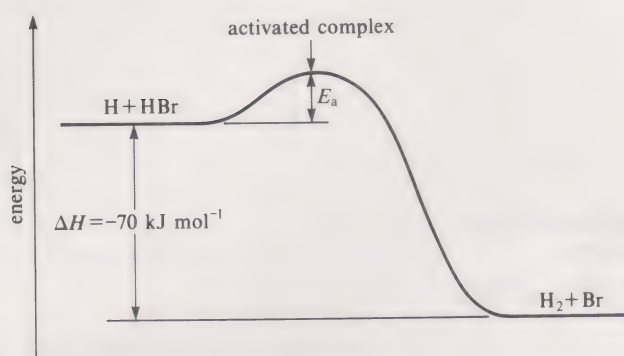


FIGURE 12 Reaction-coordinate diagram for the reaction



Again, any simple exothermic reaction will have a reaction-coordinate diagram similar to that in Figure 12. Notice that the general shape of Figure 12 is the reverse of the diagram for an endothermic process.

However, for the simple examples discussed in this Section it is possible to go one step further. Consider the two reactions together:



If the path taken by the forward reaction is the same as that taken by the reverse reaction, then it is possible to combine the diagrams in Figures 11 and 12 as shown in Figure 13. In this diagram $E_a(23)$ and $E_a(24)$ are the activation energies for the forward and reverse reactions, respectively.

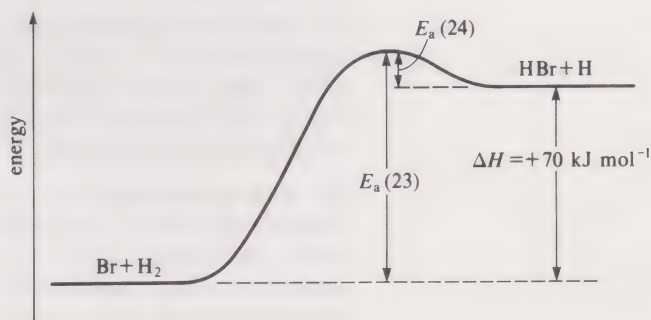
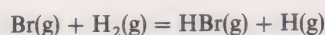


FIGURE 13 Reaction-coordinate diagram for the reaction



$E_a(23)$ and $E_a(24)$ are the activation energies for the forward and reverse reactions, respectively.

- Recalling that $E_a(23)$ is about 82 kJ mol^{-1} , can you see how Figure 13 enables you to calculate $E_a(24)$?
- It should be clear from Figure 13 that ΔH for the forward reaction is given by the difference:

$$\Delta H(23) = E_a(23) - E_a(24)$$

Thus

$$\begin{aligned} E_a(24) &= E_a(23) - \Delta H(23) \\ &= (82 - 70) \text{ kJ mol}^{-1} \\ &= 12 \text{ kJ mol}^{-1} \end{aligned}$$

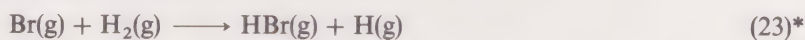
Provided that the same energy diagram applies, as here, then the expression given above is a completely general result; that is

$$\Delta H = E_{a,f} - E_{a,r} \quad (25)$$

where $E_{a,f}$ is the activation energy for the forward reaction, and $E_{a,r}$ that for the corresponding reverse reaction.

5.4 THE RATE OF REACTION AND THE ACTIVATION ENERGY

We began Section 5 by saying that, in contrast to the equilibrium constant and the overall energy change, the rate of a reaction depends on *how* the reaction actually occurs at the molecular level, that is, on the route it takes—its mechanism. In Section 5.3 you met one path or mechanism for the simple gas reaction



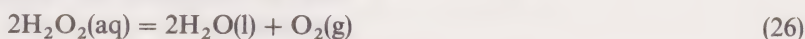
Remember that the activation energy for this reaction is found experimentally to be about 82 kJ mol^{-1} .

Compare this value with the bond dissociation energy for H_2 , $D(\text{H}-\text{H}) = 436 \text{ kJ mol}^{-1}$. Can you draw any conclusions from this comparison?

On the one hand, these values show that the activation energy is much *less* than the energy required to break the $\text{H}-\text{H}$ bond. This suggests that if the $\text{H}-\text{Br}$ bond is forming *at the same time* as the $\text{H}-\text{H}$ bond is breaking, the energy required is much less than that required to break the $\text{H}-\text{H}$ bond alone. On the other hand, the experimental value of E_a immediately rules out a possible alternative mechanism, in which H_2 molecules are first completely dissociated into H atoms: such a mechanism requires E_a to be equal to $D(\text{H}-\text{H})$, about five times as big as the experimental value. This is not surprising. The alternative mechanism suggested above would obviously be much more 'expensive' in energy terms, and it is generally true that a reaction will follow the path that involves the lowest energy barrier.

In summary: the mechanism, or path of the reaction, determines the height of the energy barrier; at a given temperature, the value of E_a has a strong influence on the speed of the reaction. It follows that a reaction will go faster if a mechanism involving a lower activation energy can be found. This can be achieved by performing the reaction in the presence of a **catalyst**, if one can be found. A catalyst is a substance that speeds up a reaction, usually without being consumed itself.

An example is the decomposition of hydrogen peroxide, H_2O_2 , a reaction that you came across in SAQ 5. A concentrated aqueous solution of hydrogen peroxide is stable at ordinary temperatures. But add a few drops of an aqueous solution containing the iron(II) ion, $\text{Fe}^{2+}(\text{aq})$, and the hydrogen peroxide rapidly decomposes to water and oxygen gas:



The presence of $\text{Fe}^{2+}(\text{aq})$ speeds up the decomposition, even though it does not appear in the balanced equation for the reaction: Reaction 26 is *catalysed* by $\text{Fe}^{2+}(\text{aq})$. A few drops of blood(!) have a similar effect, as does the addition of a lump of solid manganese dioxide (MnO_2). In the latter case, when Reaction 26 reaches equilibrium, the lump of MnO_2 remains, its mass unchanged. It speeds up the decomposition of H_2O_2 without being consumed itself: MnO_2 is also an effective catalyst for this reaction.

The study of catalysis is a subject in itself and, as the examples above suggest, the types of catalyst vary enormously. Later in this Course (Unit 22), you will meet some of the important biological catalysts, known collectively as *enzymes*. (It is an enzyme in your blood that catalyses the decomposition of hydrogen peroxide.) These are efficient (and very specific) catalysts, but they normally function only within a limited range of temperature.

Catalysts will not be discussed further in this Unit, other than to point out that the role of a catalyst is to increase the *rate* of a reaction, usually by changing the mechanism. In general, the resulting mechanism must have a lower activation energy than that without the catalyst if an increase in rate is to occur: this is illustrated schematically in Figure 14 for a hypothetical exothermic reaction, and symbolically in Figure 15. It follows from the picture in Figure 14 that a catalyst lowers the energy barrier for *both* the forward *and* the reverse reactions, and hence increases the rates of both. Thus, it does not affect the equilibrium position, but simply increases the rate at which this is attained: it *cannot* alter the value of the equilibrium constant for a reaction.

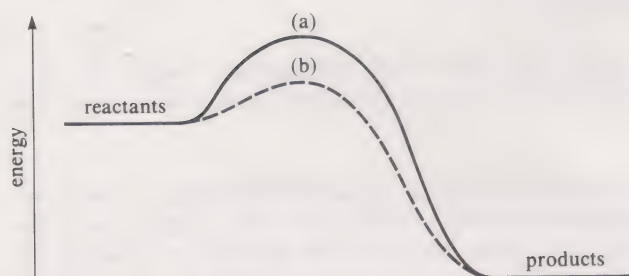


FIGURE 14 Schematic diagram to show the effect of a catalyst on the activation energy for a reaction: (a) without a catalyst; (b) in the presence of a catalyst.

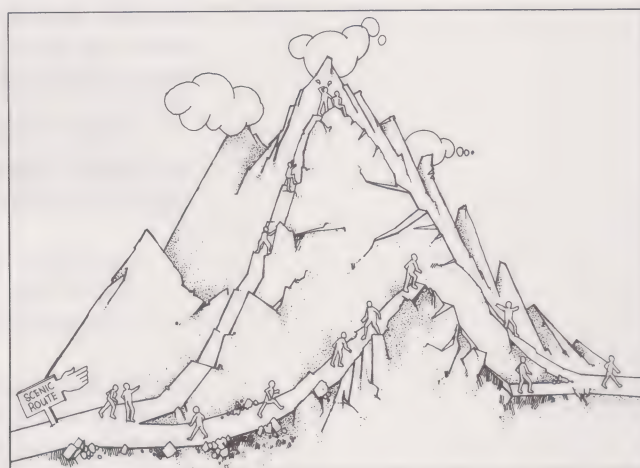
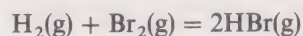
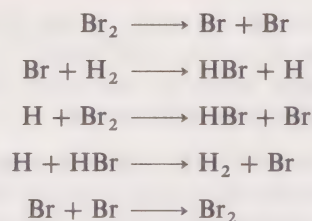


FIGURE 15 A catalyst usually helps to lower the energy barrier between reactants and products.

There is one final question we should examine before closing this Section. Throughout, we have used as examples a few very simple gas reactions: how applicable are the ideas developed here to other, more complex, reactions? The most important point is that the balanced equation for a reaction does not automatically say anything about its mechanism: this can only be inferred from the *observed* influence of concentration, temperature, etc., on the actual rate of reaction. For example, the rate of the following, and apparently simple, gas reaction



is actually found to have a highly complex dependence on the concentrations of both reactants *and* product. The reason for this is that the reaction does not take place via simple collisions between H_2 and Br_2 molecules. Rather, it involves a series of simpler reactions, two of which have been used as examples in this Section (Equations 23 and 24); the steps are listed as follows:



Do not spend time trying to work out how this sequence of reactions eventually leads to the product, HBr: it is a little complicated. The sequence is included simply to illustrate the meaning of the terms 'mechanism' and 'steps' in a complex reaction. It is usually true, however, that for *each* of the steps in a complex reaction like this, there will be:

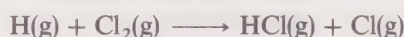
- (a) a lowest energy path for reaction
- (b) an energy barrier, and hence
- (c) an activation energy.

SUMMARY OF SECTION 5

- 1 A simple collision model accounts in a qualitative way for the observed influence of concentration and temperature on the rate of a simple gas reaction.
- 2 A more quantitative treatment highlights certain limitations of this simple model. An examination of the discrepancies between the calculated and observed rate behaviour leads to a plausible modification of the simple collision model: a collision between reactant molecules leads to reaction only when its energy is at least as great as some threshold energy, known as the activation energy.
- 3 The activation energy can be pictured as an energy barrier that reactant molecules must surmount before products can be formed.
- 4 The height of the energy barrier, and hence the rate of a reaction, depends on the mechanism of the reaction—the path by which reactants are converted into products.
- 5 When a chemical reaction is inconveniently slow, it is sometimes possible to find a catalyst. This is a substance that speeds up the reaction, usually without being consumed itself. It changes the mechanism of the reaction, and lowers the energy barrier, without affecting the equilibrium position.

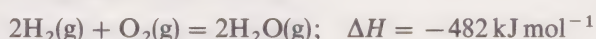
SAQ 8 State the deficiencies of a simple collision model for chemical reactions, and explain briefly how these deficiencies are overcome by the idea that reactant molecules must collide with sufficient energy (the activation energy) for reaction to occur.

SAQ 9 Consider the following gas reaction:



- (a) What is the overall enthalpy change for the reaction? Is it endothermic or exothermic?
- (b) Sketch a reaction-coordinate diagram for this reaction, and show ΔH and E_a on your sketch.
- (c) What is the value of the activation energy E_a for this reaction?

SAQ 10 As you should have found in answering ITQ 6, the following reaction is highly exothermic:



Although the value of the equilibrium constant for this reaction is very large ($K = 3.3 \times 10^{81} \text{ mol}^{-1}$ at 25°C), a gaseous mixture of hydrogen and oxygen shows no noticeable reaction under normal conditions. Can you suggest a possible reason?

However, if the mixture is passed over a mesh of platinum gauze, the reaction above proceeds rapidly. What is the role of the platinum gauze? Does its presence affect the overall enthalpy change, or the equilibrium position for the reaction?

6 REQUIREMENTS FOR REACTION TO OCCUR

Having studied Units 15 and 16, you have now met, in general terms, most of the factors that influence the progress of a chemical reaction. For a reaction to be observed to occur:

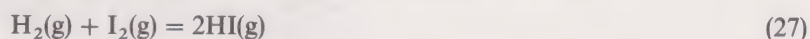
- 1 The reactant molecules must meet (collide);
- 2 The molecules must meet with sufficient energy to react (the activation energy);
- 3 The equilibrium constant must be sufficiently large to *allow* enough reaction to occur for it to be detected.

Requirement 1 is clearly affected by concentration; the more molecules there are in a given volume, the more likely they are to meet.

Requirement 2 depends on the mechanism(s) available to the reactants and, of course, on the temperature: this was the basis for the discussion in Section 5.4.

Requirement 3 cannot be altered at a given temperature, a fact that was emphasized in Section 9 of Unit 15.

But how does a *change* in the reaction conditions affect each of these requirements? First, increasing the concentration of the reactants increases the chance of requirement 1 being met, and hence generally increases the rate of the reaction. It also affects the equilibrium position. For example, consider again the reaction discussed in Section 7 of Unit 15:



for which

$$\begin{aligned} K &= \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} \\ &= 54.3 \text{ at } 427^\circ\text{C} \end{aligned} \quad (28)$$

Suppose that you have an equilibrium mixture of H_2 , I_2 and HI at a constant temperature of 427°C .

☐ What will be the effect of adding more of one reactant, hydrogen say, to this mixture?

■ Addition of H_2 will *disturb* the equilibrium: $[\text{H}_2(\text{g})]$ is increased, but the ratio of concentrations on the right-hand side of Equation 28 *cannot* change. As you saw in Unit 15, the system responds to this disturbance: more H_2 and I_2 react to form HI , thus maintaining the ratio of concentrations at its equilibrium value.

In terms of Le Chatelier's principle, the equilibrium in Equation 27 is shifted to the right, thereby increasing the equilibrium yield of HI .

☐ Can you think of another way of displacing the equilibrium, and thus increasing the equilibrium yield of product(s) at constant temperature?

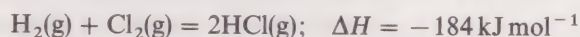
- The simplest technique, in principle, is to remove product as it is formed. Again this does not constitute a change in K . (See the answers and comments to SAQs 8 and 19 in Unit 15.)

What about the effect of changing the temperature? Well, increasing the temperature increases the chance of reaction by meeting requirement 2 above: most reactions go faster at higher temperatures.

But how does a change in temperature affect the equilibrium position? It is time to return to the question which was left unanswered at the end of Unit 15 (Section 9). There we simply noted that the equilibrium constant for a reaction may either increase or decrease as the temperature is raised. You are now in a position to predict the way the equilibrium constant varies with temperature: it depends solely on the *sign* of the enthalpy change for the reaction, that is, on whether the reaction is endothermic or exothermic.

You can see that this connection is plausible by applying Le Chatelier's principle. In this case the external constraint is an increase in temperature. Now you saw in Section 2 that the initial temperature change resulting from a reaction depends on whether the reaction is exothermic or endothermic. An exothermic reaction leads to a temperature increase; an endothermic reaction to a temperature decrease. So when the external constraint is an increase in temperature, the constraint can be lessened if the equilibrium shifts in the direction in which the reaction is endothermic, because this shift would, by itself, tend to lower the temperature. Thus, if we write down a reaction that is endothermic in the left \rightarrow right direction, the constraint imposed on the system by increasing the temperature will be reduced by the formation of more products, which corresponds to an *increase* in the value of the equilibrium constant. The reverse is true for a reaction that is exothermic in the left \rightarrow right direction: an increase in temperature causes a *decrease* in K .

ITQ 7 The enthalpy change for the following reaction was given earlier:



How will the equilibrium constant for this reaction vary with temperature?

- ☐ When will the effects of increasing temperature on requirements 2 and 3 above work in opposite directions?
- When the reaction is exothermic. Then, increasing the temperature will reduce the size of K , and hence the maximum possible yield of product, no matter how much more quickly this is formed.

As you will see in the next Section, this dilemma is commonly encountered with slow exothermic reactions in the chemical industry: one can speed the reaction up by increasing the temperature, but only at the cost of reducing the yield. One way of escape is to search for a suitable catalyst, which will speed up the reaction (generally by decreasing the activation energy) without the temperature having to be raised unduly.

SUMMARY OF SECTION 6

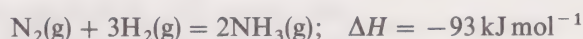
- For a reaction to be observed to occur:
 - The reactant molecules must meet (collide);
 - The molecules must meet with sufficient energy to react (the activation energy);
 - The equilibrium constant must be sufficiently large to *allow* enough reaction to occur for it to be detected.
- The rate of a reaction can generally be increased by increasing either the concentration(s) of reactant(s) or the temperature.

3 At a given temperature, the equilibrium yield of product can only be increased by displacing the equilibrium in some way.

4 The effect of temperature on the equilibrium constant (and hence equilibrium yield of product) depends on the sign of the enthalpy change for the reaction.

The following SAQ leads in to the discussion of the Haber process in the following Section, so make sure you try it.

SAQ 11 The Haber process for ‘fixing’ molecular nitrogen from the atmosphere centres around the manufacture of ammonia via the following reaction:



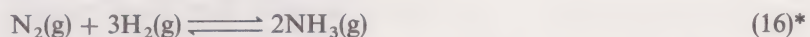
where ΔH is the enthalpy change. At 25°C the equilibrium constant for this reaction has the value $K = 2.7 \times 10^8 \text{ l}^2 \text{ mol}^{-2}$. But no appreciable reaction occurs at room temperature and pressure. In what ways could the yield of ammonia be increased?

7 THE HABER–BOSCH PROCESS

It seems fitting to close these two Units with a brief examination of an industrial process that not only has had a profound impact on our society, but also arose from a painstaking application of the scientific principles discussed in Units 15 and 16.

During the 19th century, the increase in world population was such that there was a dramatic increase in the demand for ‘fixed’ nitrogen, that is nitrogen in a chemically combined form, especially for use in fertilizers. By the turn of the century, it was recognized that the obvious place to start was the air, with its virtually unlimited supply of molecular nitrogen, free for the taking. However, the problem was more easily recognized than solved, for one of the main characteristics of molecular nitrogen (N_2) is its comparative unreactivity. As we said in Section 3.1, this can largely be attributed to the great strength of the $\text{N}\equiv\text{N}$ bond in molecular nitrogen. Nitrogen is not as unreactive as the noble gases; indeed, many thousands of nitrogen compounds are known. Nevertheless, under ordinary conditions it reacts with very few substances. Thus, the problem was to induce the unreactive nitrogen to form a compound that could be a source of fixed nitrogen suitable for both agricultural and industrial purposes. One obvious candidate was ammonia, NH_3 .

Despite its apparent simplicity, the direct synthesis of ammonia from the elements, Equation 16, proved elusive:



Fritz Haber (Figure 16), who was Professor of Technical Chemistry at Karlsruhe in Germany, came to the ammonia problem in 1903. In spite of early setbacks and much contemporary criticism from the scientific community, Haber and his colleagues persevered. They carried out a systematic investigation of the reaction and its response to changing conditions. By 1909 they had developed the essential features of a practical process, and the main principles of their designs are still in use today—quite an achievement!

Having worked through SAQ 11, you will already have an idea of the basic requirements. To summarize: the value of the equilibrium constant at 25°C ($K = 2.7 \times 10^8 \text{ l}^2 \text{ mol}^{-2}$) suggests that the equilibrium yield of ammonia should be appreciable: but the reaction is so slow at this temperature that it cannot be observed—it never reaches equilibrium. The rate of reaction can be increased by raising the temperature; but the reaction is exothermic ($\Delta H = -93 \text{ kJ mol}^{-1}$), so the maximum possible yield falls off with increas-



FIGURE 16 Fritz Haber (1868–1934) received a Nobel Prize for Chemistry in 1919 for work that led to the development of a process for the industrial synthesis of ammonia.

TABLE 5 Equilibrium yield of ammonia as a function of temperature

Temperature/°C	NH ₃ at equilibrium (%)
100	79.6
200	29.4
300	6.0
400	1.5
500	0.5

ing temperature. In this particular case, the effect is quite dramatic, as you can see from Table 5: this gives the equilibrium yield of ammonia as a percentage from an initial mixture containing N₂ and H₂ in the ratio 1:3.

Thus, a compromise has to be reached between a reasonable rate of formation of ammonia, which requires a high temperature, and an acceptable equilibrium yield, which demands a low temperature. As mentioned earlier, this conflict is common in the chemical industry, but can often be resolved by the development of a suitable catalyst.

You have also seen that the reaction in Equation 16 can be driven in the desired direction by removing ammonia as it is formed. However, there is another, and crucially important, way of displacing an equilibrium like this.

In Units 13–14 you met *Avogadro's hypothesis*: 'equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules.' A direct deduction from this hypothesis is that a mole (6×10^{23} molecules) of any gas, under the same conditions of temperature and pressure, must always have the same volume. It follows that at constant temperature and pressure, the volume on the left-hand side of Equation 16 must be twice that on the right-hand side:



You are probably familiar with the idea a gas responds to the external constraint of an increase in the external pressure by contracting—by a decrease in volume.

- Using Le Chatelier's principle, can you predict the effect of increasing pressure on the equilibrium in Equation 16?
- According to Le Chatelier's principle, the influence of an *increase* in pressure will be lessened by a *reduction* in the volume. The equilibrium will shift to the side having the *smaller* volume—the right-hand side in this case.

In general, the side having the smaller number of moles of *gaseous* molecules is favoured by an increase in pressure. Notice that this does not constitute a change in the equilibrium constant: the latter depends *solely* on the temperature.

The effect of pressure on the equilibrium yield of ammonia is shown in Table 6: the corresponding values in Table 5 are for a pressure of one atmosphere (1 atm), effectively the pressure of the atmosphere at sea-level. Thus 25 atm, for example, represents a pressure about 25 times as great as that of the atmosphere. This was the extra factor that spelt success for Haber and his colleagues. Even in the presence of a catalyst, it was necessary to raise the temperature to a point at which the yield of ammonia was disappointingly poor at atmospheric pressure. The yield was improved to a commercially viable level by working at higher pressures. Even here, however, there is a need for compromise: although an increase in pressure favours the formation of ammonia, working on an industrial scale at high

TABLE 6 Equilibrium yield of ammonia as a function of temperature and pressure*

Temperature/°C	NH ₃ present at equilibrium (%)				
	25 atm	50 atm	100 atm	200 atm	400 atm
100	91.7	94.5	96.7	98.4	99.4
200	63.6	73.5	82.0	89.0	94.6
300	27.4	39.6	53.1	66.7	79.7
400	8.7	15.4	25.4	38.8	55.4
500	2.9	5.6	10.5	18.3	31.9

* These values were taken from an article by S. P. S. Andrew, in *The Modern Inorganic Chemicals Industry* (1977), ed. R. Thompson, Special publication No. 31, The Chemical Society, London.

pressures involves engineering and technical problems, and the actual pressure employed is largely dictated by economic considerations.

Overall, then, the Haber process represents a series of informed compromises based on data obtained from many thousands of experiments. (In the commercial development of the process, led by the engineer, Carl Bosch, with the German company Badische Anilin und Soda Fabrik AG, some 6 500 experiments were carried out between 1910 and 1912 in order to find the most suitable catalyst!) Today, the process is run at a temperature in the range 400–540 °C and a pressure in the range 80–350 atm, in the presence of an activated iron catalyst containing small amounts of, typically, potassium, aluminium, silicon and magnesium oxides. In practice, the gases are circulated continually through a bed of the catalyst at such rates that the reaction does not reach equilibrium: the conversion per pass is generally quite low. However, the ammonia is condensed out of the gas stream, and the unchanged hydrogen and nitrogen are recirculated. The ammonia can then be combined with nitric or sulphuric acid to make the solid fertilizers, ammonium nitrate (NH_4NO_3) and ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$).

SUMMARY OF SECTION 7

1 The manufacture of nitrogen fertilizers depends upon the synthesis of ammonia from nitrogen and hydrogen, but at normal temperatures and pressures, the reaction is too slow.

2 Because the reaction is exothermic, too large an increase in temperature leads to an unacceptable lowering of the equilibrium yield.

3 With an iron catalyst, the rate is satisfactory at 400–540 °C, and so is the ammonia yield if the pressure of the gas mixture is raised to 80–350 atm.

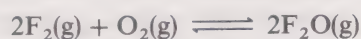
SAQ 12 The nitrogen for the Haber process is freely available in the air, but what about the hydrogen? One source that is used in modern plants is natural gas (mainly methane), which reacts with steam as follows:



(a) A Lewis structure for carbon monoxide is harder to draw than the examples of Units 13–14. However, it shows that there is a triple bond in the carbon monoxide molecule. Given that the bond energy of this $\text{C}\equiv\text{O}$ bond is $1\,076\text{ kJ mol}^{-1}$, what is the enthalpy change for the above reaction?

(b) What will be the effect of changing temperature and pressure on the yield of hydrogen from this reaction?

SAQ 13 Consider the following gaseous equilibrium



where $\Delta H = -43.5\text{ kJ mol}^{-1}$.

(a) Write an expression for the equilibrium constant of this reaction. If concentrations are expressed in mol l^{-1} , what units does K have?

(b) What effect would the following changes have on the amount of F_2O present at equilibrium?

(i) O_2 is added.

(ii) The temperature is raised.

(iii) The volume of the container is reduced (but the total amount of material does not change).

(iv) An effective catalyst is added.

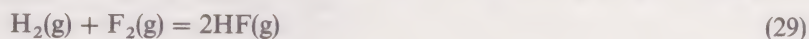
8 TV NOTES: ENERGY AND ROCKETS

This programme examines the criteria for a good rocket propellant—a particular combination of fuel plus oxidizer used for rocket propulsion. The main emphasis is on the question ‘What makes a reaction exothermic?’, and the treatment aims to reinforce that in Sections 3.1 and 3.2.

The programme began with Dr Logan demonstrating the spectacular, and obviously exothermic, reactions of dinitrogen tetroxide (N_2O_4) with two other substances—aniline and unsymmetrical dimethylhydrazine (UDMH for short). As Dr Logan’s model suggested, the second reaction ($\text{N}_2\text{O}_4 + \text{UDMH}$) has indeed been used for propulsion, chiefly in the small lateral rocket motors used to adjust the orbit of the lunar module during the Apollo Moon shots.

We then went on to examine the three general properties that any good rocket propellant must have. In summary, these are as follows:

1 *The reaction between the components must be highly exothermic* (That is, ΔH should be large and negative). We used the following simple example:



to establish that a reaction will be exothermic if it results in the formation of strong bonds at the expense of breaking weaker ones.

As mentioned above, the meaning and use of bond energies are discussed in more detail in Section 3, and a parallel discussion of more conventional chemical fuels is given in Section 4. Don’t worry if the actual calculation of the overall energy change for Reaction 29 seemed a bit too quick: it is repeated in ITQ 4.

2 *The reaction between the components must be fast.* We deduced this criterion from the great simplicity of the ‘business end’ of a rocket motor—the combustion chamber and exhaust nozzle (see Figures 17 and 18, for example.) The combustion chamber is just a hollow tube, and the reactants would simply be swept away if the reaction between them were not effectively instantaneous. All of the reactions you saw certainly fulfilled this criterion, as well as the one above.

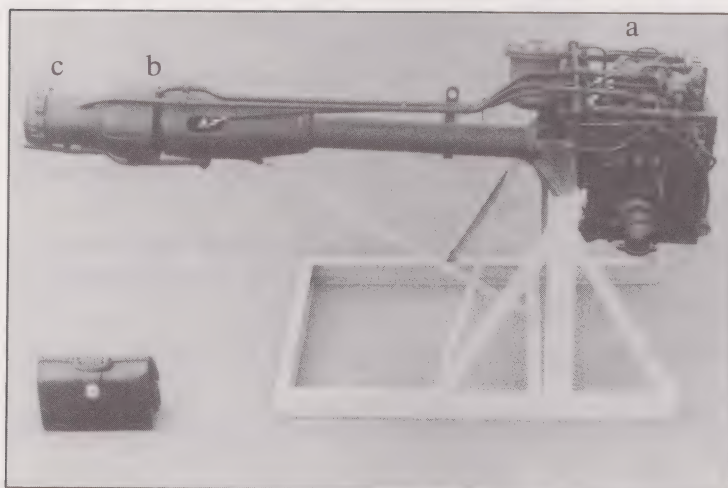


FIGURE 17 The Walter 509 rocket engine from the Messerschmidt 163: (a) pumping mechanism for delivering fuel and oxidizer to the combustion chamber; (b) combustion chamber; (c) exhaust nozzle.

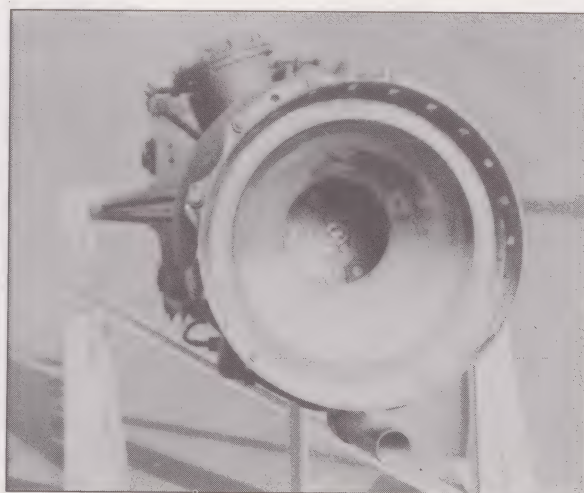


FIGURE 18 End-on view of the Walter 509 engine, showing inlet valves to the combustion chamber.

3 *The products of the reaction should be gases of low molar mass.** In a rocket engine, chemical energy is converted *directly* into kinetic energy of the product molecules in the combustion reaction. The net result is a stream

* Please forgive the anachronism of ‘molecular weight’ for ‘molar mass’ that slipped in towards the end of the programme!

of hot, fast-moving gases that are ejected through the exhaust nozzle in one direction. The 'reaction' to this causes the body of the rocket to move in the opposite direction, for much the same reason as a rifle 'kicks back' when fired (Figure 19).

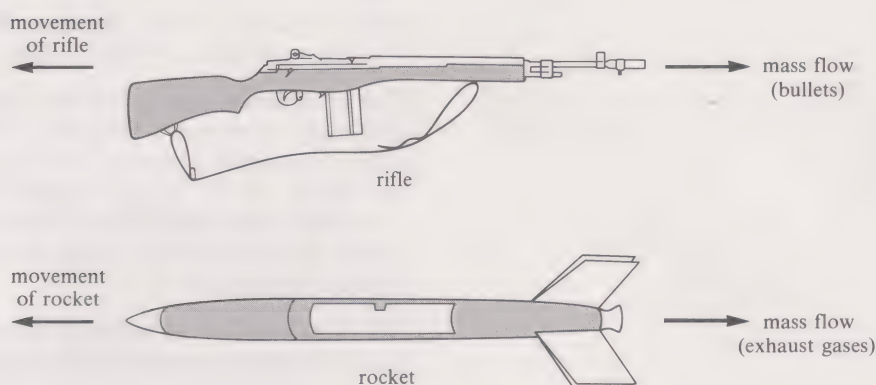


FIGURE 19 A comparison of the motion of a rocket and the recoil of a rifle. In both instances momentum is conserved: the momentum of the bullet (exhaust gases) is equal in magnitude, but of opposite sign, to the momentum of the rifle (rocket).

Although we did not discuss it in the programme, this is a further example of the law of conservation of momentum, which you met in Unit 3. Thus, if the rocket is stationary when the engine is fired,

$$\begin{aligned}\text{momentum of rocket} &= -\text{momentum of exhaust gases} \\ &= -m_e v_e\end{aligned}$$

where m_e is the mass and v_e the speed of the exhaust gases. As the minus sign implies, the rocket moves in the opposite direction to the exhaust stream.

But a rocket has to carry its own propellant, so we obviously want as large a momentum as possible per unit mass of propellant burned. In other words, one important criterion for a good rocket propellant is the size of the exhaust speed, v_e .

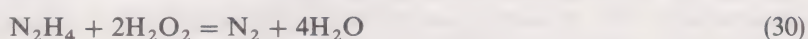
The simple demonstration you saw in the programme showed that, under identical conditions, a balloon of hydrogen (molar mass = 2 g mol^{-1}) emptied a lot faster than one containing the same amount of carbon dioxide (molar mass = 44 g mol^{-1}). In other words, the lower the molar mass, the higher the exhaust speed.

The final part of the programme showed these criteria in action in one of the forerunners of today's interplanetary rockets—the Messerschmidt 163. The propellant was as follows:

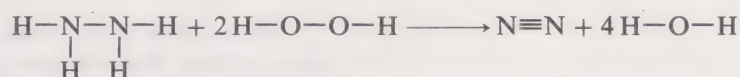
oxidizer (T-Stoff): an 80% aqueous solution of hydrogen peroxide (H_2O_2)

fuel (C-Stoff): a solution of hydrazine (N_2H_4) in methanol (methyl alcohol)

The reaction between these components produces nitrogen and steam:



or, using dashes to represent bonds,



We showed that this particular combination does have the three properties outlined above:

- 1 In Reaction 30, some weak bonds (especially O—O and N—N) disappear, and they are replaced by strong ones (N≡N and O—H): the reaction is highly exothermic. The calculation of ΔH for this reaction is part of SAQ 7.
- 2 You saw that the reaction is very fast.
- 3 The products have relatively low molar masses: both are less dense than air.

OBJECTIVES FOR UNIT 16

After you have worked through this Unit, you should be able to:

- 1 Explain the meaning of, and use correctly, all the terms flagged in the text.
- 2 Given the value of the enthalpy change for a reaction, decide whether the reaction is endothermic or exothermic, and hence whether heat will be absorbed or released at constant temperature. (*ITQ 4; SAQs 1, 5, 7, 9, 11, 12 and 13*)
- 3 Decide whether a given phase change is either exothermic or endothermic. (*ITQ 2; SAQs 2 and 3*)
- 4 Draw Lewis structures (or recognize correct structures) for simple gas molecules and hence list the bonds broken and formed in a given gas reaction. (*ITQs 3, 5 and 6; SAQ 4*)
- 5(a) Given a Table of bond energies or average bond energies, together with the information in Objective 4, calculate the enthalpy change for a simple gas reaction. (*ITQs 4 and 6; SAQs 4, 5, 9 and 12*)
- (b) Using Hess's law and appropriate enthalpies for phase changes, extend the procedure in (a) to the calculation of enthalpy changes for reactions involving liquids or solids. (*SAQs 4 and 5*)
- 6 Explain the limitations of the procedure outlined in Objective 5. (*SAQ 6*)
- 7 Use the procedure outlined in Objectives 4, 5 and 6 to discuss:
 - (a) the combustion of a typical chemical fuel in oxygen;
 - (b) the reaction of a typical fuel and oxidizer used for rocket propulsion. (*TV; SAQs 4 and 7*)
- 8 Explain in general terms how a collision model of chemical reactions, together with the idea of a threshold or activation energy, accounts for the observed influence of concentration and temperature on the rate of a reaction. (*SAQ 8*)
- 9(a) Sketch (or recognize a correct sketch of) the reaction-coordinate diagram for a simple reaction of given ΔH .
- (b) Using such a sketch, distinguish between the enthalpy change for a reaction and its activation energy. (*SAQ 9*)
- 10 Relate the role of a catalyst to a reaction-coordinate diagram. (*SAQs 10 and 13*)
- 11 Describe, in terms of Le Chatelier's principle, how the equilibrium constant varies with temperature for (a) exothermic reactions, and (b) endothermic reactions. (*ITQ 7; SAQs 11, 12 and 13*)
- 12 List the requirements for a chemical reaction to occur and hence:
 - (a) predict the effect of changing reaction conditions (for example, temperature and pressure) on the progress of a given reaction;
 - (b) show how these factors influence the choice of reaction conditions for a given industrial process. (*SAQs 11, 12 and 13*)

ITQ ANSWERS AND COMMENTS

ITQ 1 1 200 kJ. You want to vaporize 500 cm^3 , that is 500 g, of water.

The molar mass of H_2O is $(2 + 16)\text{ g} = 18\text{ g}$.

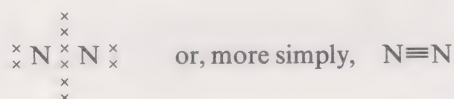
So 500 g represents $\frac{500}{18}$ mol of H_2O .

To vaporize 1 mol requires 43.3 kJ.

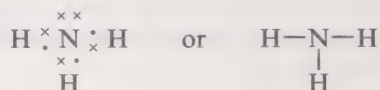
So $\frac{500}{18}$ mol require $\frac{500}{18} \times 43.3\text{ kJ} \approx 1\,200\text{ kJ}$.

ITQ 2 Yes. The endothermic process $\text{ether(l)} \rightarrow \text{ether(g)}$ takes energy from its surroundings, including your skin, and so leaves you feeling colder.

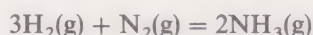
ITQ 3 As you saw in Units 13–14, nitrogen has five electrons in its outermost shell. In N_2 each nitrogen atom can attain a noble gas structure by sharing *three* pairs of electrons:



Similarly, in NH_3 , all the atoms can attain noble gas structures by sharing pairs of electrons:

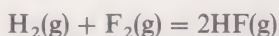


(Remember, structures like this are simply a representation of the bonds present in the molecule, and do not reflect the actual shape of the molecule.) Thus, in the reaction given,



three H—H bonds and one $\text{N} \equiv \text{N}$ bond are broken for every six N—H bonds formed.

ITQ 4 In the reaction

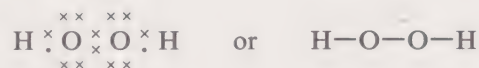


one H—H and one F—F bond are broken for every two H—F bonds formed. The reaction is very similar to the one discussed in the text. Thus

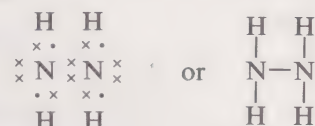
$$\begin{aligned} \Delta H &= D(\text{H}-\text{H}) + D(\text{F}-\text{F}) - 2D(\text{H}-\text{F}) \\ &= (436 + 158 - 2 \times 568)\text{ kJ mol}^{-1} \\ &= -542\text{ kJ mol}^{-1} \end{aligned}$$

The reaction is strongly exothermic, largely because it results in the formation of very strong H—F bonds at the expense of breaking weaker ones. Indeed, the weakness of the F—F bond suggests why many reactions with fluorine are strongly exothermic (see Section 4).

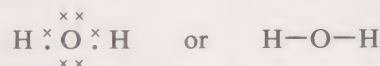
ITQ 5 Oxygen has six electrons in its outermost shell, and hydrogen has one, so in H_2O_2 each atom can attain a noble gas electronic configuration by sharing pairs of electrons, as:



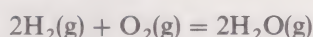
Similarly, the N and H atoms in N_2H_4 can attain noble gas electronic configurations as follows:



ITQ 6 As in ITQ 5, in H_2O each atom can attain a noble gas electronic configuration by sharing pairs of electrons, as:



In the reaction given,



two H—H bonds and one O=O bond (in O_2) are broken for every four O—H bonds formed. Thus

$$\Delta H = 2D(\text{H}-\text{H}) + D(\text{O}=\text{O}) - 4D(\text{O}-\text{H})$$

Tables 1 and 3 include values for these bond energies, whence

$$\begin{aligned} \Delta H &= (2 \times 436 + 498 - 4 \times 463)\text{ kJ mol}^{-1} \\ &= -482\text{ kJ mol}^{-1} \end{aligned}$$

The heat released is 482 kJ per mole of the reaction *as written*, that is, per two moles of hydrogen and one mole of oxygen consumed, and two moles of water vapour formed.

ITQ 7 ΔH is negative: the reaction is exothermic, so the equilibrium constant should *decrease* with increasing temperature. Le Chatelier's principle leads to this conclusion if you think of the increase in temperature as an external constraint. This constraint can be reduced if the equilibrium shifts in the endothermic direction—towards the left-hand side (reactants). This corresponds to a *decrease* in K .

- 1 In Reaction 30, some weak bonds (especially O—O and N—N) disappear, and they are replaced by strong ones (N≡N and O—H): the reaction is highly exothermic. The calculation of ΔH for this reaction is part of SAQ 7.
- 2 You saw that the reaction is very fast.
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OBJECTIVES FOR UNIT 16

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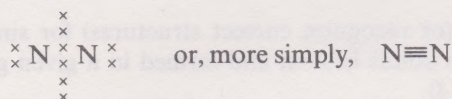
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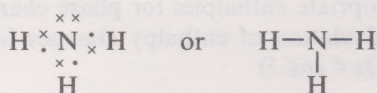
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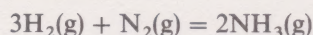
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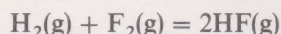


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three H—H bonds and one $\text{N} \equiv \text{N}$ bond are broken for every six N—H bonds formed.

ITQ 4 In the reaction

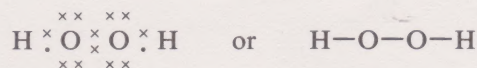


one H—H and one F—F bond are broken for every two H—F bonds formed. The reaction is very similar to the one discussed in the text. Thus

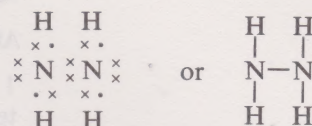
$$\begin{aligned} \Delta H &= D(\text{H}-\text{H}) + D(\text{F}-\text{F}) - 2D(\text{H}-\text{F}) \\ &= (436 + 158 - 2 \times 568)\text{ kJ mol}^{-1} \\ &= -542\text{ kJ mol}^{-1} \end{aligned}$$

The reaction is strongly exothermic, largely because it results in the formation of very strong H—F bonds at the expense of breaking weaker ones. Indeed, the weakness of the F—F bond suggests why many reactions with fluorine are strongly exothermic (see Section 4).

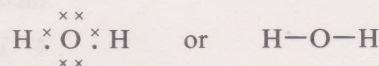
ITQ 5 Oxygen has six electrons in its outermost shell, and hydrogen has one, so in H_2O_2 each atom can attain a noble gas electronic configuration by sharing pairs of electrons, as:



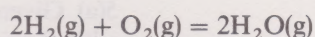
Similarly, the N and H atoms in N_2H_4 can attain noble gas electronic configurations as follows:



ITQ 6 As in ITQ 5, in H_2O each atom can attain a noble gas electronic configuration by sharing pairs of electrons, as:



In the reaction given,



two H—H bonds and one $\text{O}=\text{O}$ bond (in O_2) are broken for every four O—H bonds formed. Thus

$$\Delta H = 2D(\text{H}-\text{H}) + D(\text{O}=\text{O}) - 4D(\text{O}-\text{H})$$

Tables 1 and 3 include values for these bond energies, whence

$$\begin{aligned} \Delta H &= (2 \times 436 + 498 - 4 \times 463)\text{ kJ mol}^{-1} \\ &= -482\text{ kJ mol}^{-1} \end{aligned}$$

The heat released is 482 kJ per mole of the reaction *as written*, that is, per two moles of hydrogen and one mole of oxygen consumed, and two moles of water vapour formed.

ITQ 7 ΔH is negative: the reaction is exothermic, so the equilibrium constant should *decrease* with increasing temperature. Le Chatelier's principle leads to this conclusion if you think of the increase in temperature as an external constraint. This constraint can be reduced if the equilibrium shifts in the endothermic direction—towards the left-hand side (reactants). This corresponds to a *decrease* in K .

SAQ 10 The size of the equilibrium constant suggests that the *equilibrium* position strongly favours formation of product at 25°C. The lack of reaction must be because the rate is very low, and this suggests that the activation energy is probably high.

The platinum gauze acts as a catalyst: it changes the mechanism of the reaction, lowering the energy barrier and hence increasing the speed of the reaction. According to the simple picture in Figure 14 (Section 5.4), a catalyst affects neither the overall energy change ΔH nor the final equilibrium position; that is, the value of K does not change.

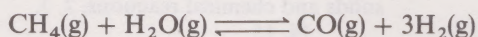
SAQ 11 As in SAQ 10, the value of K at 25°C is large, so the equilibrium position favours the formation of ammonia at this temperature. Again, the rate of reaction must be slow under normal conditions: the activation energy is high.

The rate of reaction can be increased by raising the temperature: but there is a problem. The reaction is exothermic, so K will decrease with increasing temperature: the temperature chosen will be a compromise between the need for a reasonable rate and an acceptable equilibrium yield.

If an efficient catalyst can be found, this will speed up the reaction (by lowering the energy barrier) without the temperature having to be raised unduly.

Finally, the reaction could be driven in the forward direction by removing the ammonia as it is formed. You deduced this result in answering SAQs 8 and 19 of Unit 15.

SAQ 12 (a) The reaction of interest is



in which four C—H and two O—H bonds are broken for every one C≡O bond and three H—H bonds formed. Thus

$$\Delta H = 4D(\text{C—H}) + 2D(\text{O—H}) - D(\text{C}\equiv\text{O}) - 3D(\text{H—H})$$

Taking values from Tables 1 and 3, and using the one given,

$$\begin{aligned}\Delta H &= (4 \times 416 + 2 \times 463 - 1076 - 3 \times 436) \text{ kJ mol}^{-1} \\ &= +206 \text{ kJ mol}^{-1}\end{aligned}$$

(b) The reaction is endothermic, so both the rate of reaction and the equilibrium yield of product will be increased by raising the temperature.

From the reaction equation and Avogadro's hypothesis, the volume on the right-hand side is twice that on the left. According to Le Chatelier's principle, the effect of an increase in pressure will drive the equilibrium over to the side with the smaller volume, the reactant side. So to increase the yield of hydrogen the reaction should ideally be run under low pressure.

SAQ 13 (a) $K = \frac{[\text{F}_2\text{O}(\text{g})]^2}{[\text{F}_2(\text{g})]^2[\text{O}_2(\text{g})]}$

and the units of K are

$$\frac{(\text{mol l}^{-1})^2}{(\text{mol l}^{-1})^2(\text{mol l}^{-1})} = \frac{1}{\text{mol l}^{-1}} = \text{l mol}^{-1}$$

If you had difficulty with this question, refer again to Section 7 of Unit 15.

(b) (i) If O_2 is added, the equilibrium is disturbed. According to Le Chatelier's principle, balance can be restored if the equilibrium shifts to the right, thus increasing $[\text{F}_2\text{O}(\text{g})]$.

(ii) The reaction is exothermic, so increasing the temperature will reduce the value of K and hence the equilibrium yield of F_2O .

(iii) If the *total* amount of material is constant, reducing the volume of the container increases the overall pressure. According to Le Chatelier's principle, the effect of an increase in pressure is to shift the equilibrium to the side with the smaller number of gaseous molecules, the right-hand side in this case. This increases the equilibrium yield of F_2O .

(iv) Provided the system is at equilibrium, adding a catalyst can have no effect on the yield of F_2O : a catalyst alters the rate of a reaction but not the equilibrium position.

If you had difficulty with these questions, refer again to Section 4.4 of Unit 15, and Sections 6 and 7 of Unit 16.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to the following sources for permission to reproduce illustrations in this Unit:

Figure 1 Keystone Press; *Figure 8* Billings Energy Corporation; *Figure 16* courtesy of Dr L. Haber.

We would like to thank Dr I. E. Smith of the Cranfield Institute for his help with the TV programme, and Dr J. Holloway of the University of Leicester for setting up the hydrogen/fluorine demonstration.

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